

























STATE OF CALIFORNIA  
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DEPARTMENT OF NATURAL RESOURCES  
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DIVISION OF MINES  
FERRY BUILDING, SAN FRANCISCO 11  
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FRANCISCO

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# MINERAL COMMODITIES OF CALIFORNIA

GEOLOGIC OCCURRENCE, ECONOMIC DEVELOPMENT AND  
UTILIZATION OF THE STATE'S MINERAL RESOURCES

Revision of Bulletin 156

*Prepared Under the Direction of*  
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### LETTER OF TRANSMITTAL

To THE HONORABLE GOODWIN J. KNIGHT  
Governor of the State of California

Dear Sir: I have the honor to transmit herewith Bulletin 176, *Mineral Commodities of California*, prepared under the direction of Olaf P. Jenkins, Chief of the Division of Mines, edited by Lauren A. Wright, and written mainly by staff members of the Division. This volume, although a revision of Bulletin 156 published in 1950, presents a much enlarged and almost wholly reworded text and is the most comprehensive single reference on the mineral industry of California. Bulletin 176 is being published in a period when a growing population and intensive industrialization have placed great demands on the mineral resources of the state, and when the annual mineral output of California has risen in value to about one and a half billion dollars. The commodity descriptions contained in this volume apprise the state's mineral-consuming industries of the nature and distribution of available raw materials; provide guidance to the prospector, miner, and mineral economist in developing and marketing these materials; and present a source of basic information to the general public for whose ultimate good the mining industry exists.

Respectfully submitted,

DEWITT NELSON, Director  
Department of Natural Resources

June 1, 1957.







## PREFACE

This, the second edition of *Mineral Commodities of California* has been assembled by the staff of the California Division of Mines as a general summary of the mineral resources and mineral industry of the state. Although the present volume bears the same title as its predecessor, which was published in 1950 as Bulletin 156, it retains only a small part of the original wording. Moreover, the second edition contains a much longer text and many more illustrations than the first, and an enlarged format has permitted a freer use of index and geologic maps than was possible in the smaller volume. Although most of the authors are staff members of the Division of Mines, many persons in industry and in state and federal agencies have provided much invaluable information, advice, and encouragement. Specific contributions from such sources are acknowledged from place to place within the volume, but the innumerable persons whose assistance was of a general nature must be thanked collectively.

The organization and context of both editions has been guided mainly by the nature of the many thousands of mineral commodity questions that are directed to the Division each year. These questions can be placed in two general categories: (1) those that request descriptive data on the location, physical and chemical properties, extent, and geologic setting of the various mineral commodities in the state, and (2) those asked in search of assistance in the developing, processing, and marketing of mineral materials in California.

The present volume consists of an introductory section followed, in alphabetical order, by 78 sections, each covering a mineral commodity or group of closely related commodities, and each written by one or more commodity specialists. Wherever, possible, the sections have been organized similarly and include a summary statement followed by discussions of mineralogy, general geology, occurrences in California, mining methods, treatment, utilization, marketing, and prices. The coverage of mineralogy and general geology has been kept brief to minimize the repetition of data that can be found in standard textbooks on mineralogy and economic geology. Consequently, only the more obvious and diagnostic physical properties of some commodities have been noted. Many of the discussions of general geology include descriptions of individual out-of-state deposits or districts, particularly those that contribute mineral raw materials to industries in California or whose existence, for one reason or another, has hindered or precluded the development of the same or related commodities within the state. Such out-of-state coverage is intended, therefore, to bring the mineral resources of California into proper perspective and to apprise the

potential operator in California of the general nature of the competition that he might encounter from elsewhere.

Special emphasis has been placed on the geological processes that have led to the formation of economic mineral deposits in certain terranes and in well-defined geographic belts in California. Such recognized belts are especially likely areas for prospecting, and wherever possible the authors have attempted to delineate them on the commodity location maps.

That the commodity descriptions in the present edition contain a much more thorough coverage of utilization and marketing than do those in Bulletin 156, is largely attributable to the progress being made in the Mineral Utilization Survey program of the Division of Mines. This program, which was begun in 1950, has been directed toward a better understanding of the present and potential mineral needs of the industries of California, so that the attention of industrial personnel can be directed to available raw materials, and the prospector can be made more aware of the types of materials most needed and their specifications. The ever-changing nature and the increasing complexity of the mineral market field require that this program be a continuing one. Newly acquired data thus obtained will appear in future publications of the Division of Mines.

The scope and the space limitations of Bulletin 176 have required that the subject matter be highly condensed. A rather extensive literature exists, however, for most of the commodities discussed. To the reader who seeks additional information, the bibliographies at the end of each section are commended. These bibliographies are not intended to be comprehensive, but in general list the most recent and most informative references.

To all of the authors the Editor wishes to express his personal appreciation. Their interest, cooperation, and patience with his editorial suggestions greatly facilitated his assignment. He also is indebted to numerous other staff members, who are unlisted as authors, but whose careful work has contributed in a very real way to the completion of the volume. Most of the drafted illustrations were prepared by Richard A. Crippen, Jr., and his staff, composed of Carl J. Sharits, Sylvia L. Koontz, and Margaret P. Cellarius. Especial thanks also are extended to Elisabeth L. Egenhoff and Mary H. Rice for their invaluable editorial assistance, to Henry H. Symons for providing utilization and marketing data, and to the entire stenographic staff for their efficient typing of the many manuscripts.

Lauren A. Wright  
Los Angeles, California  
April 15, 1957







# NATURAL ENVIRONMENT OF THE MINERAL RESOURCES OF CALIFORNIA

BY OLAP P. JENKINS

A study of the map of California showing the distribution of its developed mineral deposits suggests a pattern which is not haphazard, but is controlled by certain basic features. Both natural and cultural features affect the controls. Where the deposits are of commodities limited in extent and of high unit value, as are metals and fuels, their distribution is entirely controlled by natural environment. On the other hand, where the deposits represent commodities which are practically unlimited in extent, as are sand and gravel, the distribution is controlled not only by natural environment but by proximity to markets. More exacting demands in industry, however, may require improvement of grade, which is accomplished either by finding more suitable deposits at distant localities, or by processing the minerals near at hand. In general, however, the nonmetallic mineral commodities represent the more abundant resources, and a map of their distribution indicates that they cluster about the great centers of population, while the minerals of greater unit value are located only in the natural provinces suited to their environment. In consideration of the natural environment of mineral deposits, the following discussion may help to explain some of the various geologic factors involved in the commodity studies of this volume.

**Classification of Rocks.** Rock formations, in contrast to mineral deposits, are the larger geologic bodies which make up the earth's crust. A rock may be made up principally of a single kind of mineral, as, for example, dolomite, but generally it is composed of an aggregate of different kinds of minerals like feldspar, quartz, and mica, which are found in granite. Both dolomite and granite are often quarried as commodities where they are useful to industry, and the term mineral commodity as applied in this volume to include both rocks and minerals useful to industry. The following rock classifications include the most common types: I. Igneous rocks; II. Sedimentary rocks; III. Metamorphic rocks.

## I. Igneous rocks.

Volcanic rocks	Rhyolite	Andesite	Basalt
Dike rocks	Porphyritic equivalents of volcanic and granitic rocks		
Granitic rocks	Granite	Diorite	Gabbro

The more siliceous or acidic, light-colored igneous rocks comprise the rhyolite-granite class. Volcanic glasses, pumice, and perlite are in this class.

The more basic or ferromagnesian, dark-colored rocks comprise the basalt-gabbro class and the ultrabasic series of peridotites (serpentine) and pyroxenite.

## II. Sedimentary rocks and their metamorphic equivalents.

Unconsolidated	Consolidated	Metamorphosed equivalents
Gravel	Conglomerate	Conglomerate quartzite
Sand	Sandstone	Quartzite
Clay and silt	Shale	Slate, phyllite, or schist
Marl	Limestone and dolomite	Marble and crystalline limestone or dolomite

## III. Metamorphic rocks.

Various schists and gneisses formed by deep-seated alteration of either sedimentary or igneous rocks.

Often the prefix meta- is used to indicate that the rock has been altered by deep-seated pressure and heat. Schists and gneisses may be the product of metamorphism of either sedimentary or igneous rocks.

**Classification of Mineral Deposits.** Concentrations of minerals, as in the case of ore deposits, have come about in many different ways and during many different geologic periods. So far as geologic processes are concerned, they may be classified in the following manner.

### Classification of mineral deposits.

#### Sedimentary deposits

Examples: Placer deposits in streams  
Saline deposits in lakes  
Clay deposits in lagoons  
Limestone deposits in the sea

#### Residual deposits

Examples: Manganese oxide deposits, concentrated by weathering  
Clay deposits, resulting from weathering

#### Vein and replacement deposits

Examples: Shallow veins, such as cinnabar deposits  
Intermediate veins, such as along the Mother Lode  
Deep veins and irregular contact deposits, such as tungsten deposits, in the high Sierra

#### Magmatic deposits

Examples: Pegmatite bodies, containing gem minerals  
Chromite concentrations in serpentine

**The Geologic Record.** Every mineral deposit represents not only the results of geologic processes, but may be considered a page in geologic history. That page is inserted in the larger chapters written in the rock formations which make up the earth's crust.

In the formation of rocks and their associated mineral deposits, a long history is involved representing time measured in millions of years. In building up any historical record of a given area, the sequence of the rock formations must first be determined through field study of stratigraphy and structure. Each rock unit is related to the history of other rocks of the earth, and it is a remarkable fact that there are rock formations in California representing practically every major age group known. The general geologic column, or time scale, is shown in table 1.

The rocks and mineral deposits are part of the internal structure of the earth, whether they occur at depth or immediately beneath the surface. The actual surface features of the earth generally reflect this internal structure, or at least the major features of it. That is why a relief model of the State of California exhibits such interesting features, which appear to be closely related to the distribution of mineral deposits.

As the mineral deposits are associated with rock structure and the rock structure is reflected in the surface relief, all these features form a pattern which cannot be haphazard but which is controlled by natural environ-



Table I. Geologic time scale.

Possible age in millions of years	Era	Period	Epoch
0 to 60-----	Cenozoic-----	Quaternary-----	{Recent Pleistocene
		Tertiary-----	{Pliocene Miocene Oligocene Eocene Paleocene
60 to 190-----	Mesozoic-----	{Cretaceous Jurassic Triassic	
190 to 500-----	Paleozoic-----	{Permian Carboniferous-----	{Pennsylvanian Mississippian
		{Devonian Silurian Ordovician Cambrian	
500 and over-----	Pre-Cambrian-----	{Algonkian Archean	

ment. Therefore, the surface features of California, as exhibited by a relief map of the state, are the results of recent geologic processes acting upon an underlying mass of rocks formed millions of years ago.

If the surface of the earth were immovable, erosion would eventually level it down to a smooth plain, but since parts of it are frequently elevated, depressed, or displaced from other parts by deep-seated action in the earth, the effect of erosion is variable. It is accelerated on the higher places, while sediment is carried to fill up the places which are lower.

In the erosional carving of rocks of different hardness and character, an irregular surface is developed reflecting the underlying structures. Where the earth has been displaced along great earthquake faults, the rocks may be so pulverized that erosional processes wear out long, narrow valleys such as those found along the great San Andreas fault.

Maps of California showing the major structural features, the distribution of principal rock types, and the relief features, show that the state may be divided into a number of different regional provinces, each of which has distinct physical characteristics. This is further brought out when these provinces are examined in the field, and the distribution of the mineral deposits is mapped in relation to rock formations, structure, and topography.

*Geomorphic Provinces.* The distinctive natural divisions of California fall into at least 11 well-recognized physiographic or geomorphic provinces. For the sake of describing them briefly and treating them from the standpoint of their geologic growth, these 11 provinces may be grouped into five areas with somewhat similar physical features.

Group I includes three great mountain areas—the Sierra Nevada, the Klamath Mountains, and the Peninsular Ranges. All three represent positive earth elements in the evolution of the geologic past. As mountain areas, they gave source to sediments which filled basins

in the sea during Cretaceous and Tertiary periods. The basin areas were later raised above sea level and the rocks were thrown into long folds trending northwestward. These areas, now the Coast Ranges and Transverse Ranges, form the two provinces of Group II.

Today there lies between the Sierra Nevada and Coast Ranges the Great Valley of California. This basin is filled with sediments, and is drained from the north by the Sacramento River and from the south by the San Joaquin River. These rivers join in the delta area before they enter San Francisco Bay through Carquinez Strait. Farther south is another basin filled with sediments, the surface of which, over a large area, lies below sea level. This is the Colorado Desert, including the Salton Sink. It occupies a position between the Peninsular Ranges and the mountain ranges of the Mojave Desert. The Great Valley of California and the Colorado Desert form Group III.

A large area in the northeastern part of California is covered with volcanic rocks, which extend into eastern Oregon and eastern Washington, and cover in all some 250,000 square miles. For the most part, they form a plateau which, in California, is called the Modoc Plateau. Along the western margin of the Modoc Plateau high volcanic cones rise, forming the Cascade Range. In California, this range is dominated by Mt. Shasta; Lassen Peak terminates the Cascade province at its southern extremity. The Modoc Plateau and the Cascade Range are included in Group IV.

To the east of the Sierra Nevada and the Modoc Plateau, and extending far across the State of Nevada, is a geomorphic province known as the Basin Ranges. It is characterized by block-faulted mountains, separated by gravel-washed desert valleys. A portion of this province appears in the extreme northeastern corner of California where it is known as the Warner Range, and also to the east of the Sierra Nevada. The characteristic northwest trend of the Basin Ranges is terminated along the great Garlock fault, which also terminates the Sierra Nevada on the south, where the Tehachapi Mountains join the Transverse Ranges. At this point, the Garlock fault intersects the San Andreas fault and the area occupying the triangle formed between these two great faults is a characteristic desert region known as the Mojave Desert. It stretches far to the east through San Bernardino County, and to the southeast through the eastern part of Riverside and Imperial Counties. The Mojave Desert may be considered to be bounded along the southwest by the San Andreas fault. The Mojave Desert and Basin Ranges, together, form Group V. The geologic features of these desert areas are very different from those of the other provinces, and very complex.

It is logical that these geographic provinces and group of provinces, distinct as they are from each other, should contain entirely different types of mineral deposits. As a result, more mineral commodities have been developed in California than in any other area of similar extent. These are of sufficient importance to make the state nearly self-sufficient in minerals for industry. The most important mineral belts, districts, and occurrences, are grouped below by provinces and by the geologic period of their formation.





FIGURE 1.



*Geomorphic provinces of California arranged in five groups.*

- |  |             |
|--|-------------|
| 1. Sierra Nevada-----                                      | } Group I   |
| 2. Klamath Mountains-----                                  |             |
| 3. Peninsular Ranges-----<br>(including Los Angeles Basin) |             |
| 4. Coast Ranges-----                                       | } Group II  |
| 5. Transverse Ranges-----                                  |             |
| 6. Great Valley of California-----                         | } Group III |
| 7. Colorado Desert-----                                    |             |
| 8. Modoc Plateau-----                                      | } Group IV  |
| 9. Cascade Range-----                                      |             |
| 10. Basin Ranges-----                                      | } Group V   |
| 11. Mojave Desert-----                                     |             |

*Group I*

Vein and replacement deposits of the Sierra Nevada, Klamath, and Peninsular Ranges (mineralization chiefly late Jurassic and early Cretaceous)

*Sierra Nevada*

Mother Lode—East Belt—Grass Valley—Nevada City—Allegany gold-quartz district  
 Foothill copper-zinc belt and northern copper belt  
 Central-southern lead-zinc belt  
 Eastern tungsten belt  
 Southern tungsten, tin, and antimony belt  
 Chromite-bearing serpentine belts  
 Manganese-bearing cherts  
 Magnesite replacement in serpentine

*Klamath Mountains*

Gold belts  
 Shasta copper-zinc and iron belt  
 Chromite-bearing serpentine belts  
 Manganese-bearing cherts  
 Magnesite replacements in serpentine

*Peninsular Ranges*

Gold belts  
 Tin district  
 Gem-bearing pegmatite district  
 Nickel district

Oil and gas of Los Angeles Basin chiefly of Tertiary age

Limestone deposits of Paleozoic in all three provinces

Placer gold—Tertiary and Quaternary—in all three provinces

Clay, coal, and quartz sand deposits of Eocene and Paleocene (Tone and Alberhill) in all three provinces.

The Klamath Mountains and Peninsular Ranges are provinces at opposite ends of the state which have many geologic features in common with those of the Sierra Nevada. The Klamath Mountains, however, contain a section of much older rocks than any found in the Sierra Nevada. The southern Peninsular Ranges contain a large area of pegmatites not present in the northern provinces, but they do not contain chromite-bearing serpentine. The orderly arrangement of mineral zones and belts in the Sierra Nevada is much more striking than in the Klamath Mountains and Peninsular Ranges.

*Group II**Coast Ranges and Transverse Ranges*

Franciscan (Jurassic) chromite-bearing serpentine  
 Manganese-bearing Franciscan cherts  
 Magnesite replacements in serpentine  
 Quicksilver deposits in Tertiary and Quaternary rocks  
 Small pyrite and copper deposits, and a silver district in northern Coast Ranges—Tertiary  
 Very little gold in Jurassic rocks  
 Titanium deposits in San Gabriel Transverse Ranges  
 Franciscan limestone  
 Paleozoic limestone and dolomite

*Tertiary limestone*

Eocene coal, quartz sand  
 Tertiary volcanic rocks (building stone and aggregates)  
 Tertiary oil and gas fields  
 Gypsite deposits in Tertiary and Quaternary rocks  
 Marine diatomite of Tertiary age  
 Recent salines; placer gold in Transverse Ranges

In the Coast Ranges there is a central belt of old granite basement rocks, quite different from the so-called basement of Jurassic Franciscan igneous and sedimentary rocks which underlies other parts of the province. In this and other respects, the Transverse Ranges have many of the same characteristics as the southern Coast Ranges, but their structural trend is westward rather than northwestward. The large oil and gas fields of the state are grouped near each other: in the southern Coast Ranges, Transverse Ranges, Los Angeles Basin, and southern San Joaquin Valley.

*Group III**Great Valley of California*

Oil and gas of Tertiary age  
 Gas of Cretaceous age  
 Colorado Desert (sometimes included with group V)  
 Carbon-dioxide gas

The Great Valley is a large province enclosed by high mountains with distinct characteristics, but judged as an oil and gas province, it may be likened somewhat to the Los Angeles Basin, which lies between the Peninsular Ranges and the Transverse Ranges. The Colorado Desert is a basin filled with sediments, but these sediments are of different character than those of the Great Valley.

*Group IV**Cascade Range and Modoc Plateau*

Pumice and perlite deposits  
 Freshwater diatomite of Tertiary age

The Modoc Plateau and the Cascade Range are volcanic provinces, and represent extensions of similar provinces southward from Oregon. The volcanic rocks cover a basement which should connect the Sierra Nevada with the Klamath Mountains.

*Group V**Basin Ranges and Mojave Desert**Tertiary and Quaternary*

Complex metalliferous deposits, gold and silver, etc.  
 Epithermal manganese deposits  
 Strontium, borax, and various salines  
 Sulfur and gypsum deposits  
 Gold and tungsten placers

*Late Jurassic and early Cretaceous*

Complex metalliferous deposits (gold, silver, lead, zinc, copper)  
 Lead and zinc of Darwin-Cerro Gordo district  
 Tungsten deposits of Bishop district  
 Iron deposits, some of doubtful age

*Paleozoic and older*

Limestone and some dolomite deposits

*Pre-Cambrian*

Tale deposits of Death Valley area  
 Rare earth metals  
 Andalusite deposits of White Mountains

*Age unknown*

Rare earth metals of Clark Mountain



The Basin Ranges and the ranges of the Mojave Desert all represent a mountainous desert region which has somewhat similar geologic features, but which is quite distinct from all other sections of the state. The oldest rocks of the geologic column occur in these provinces. Marine Cretaceous and Tertiary are lacking, but much of the mineralization is Tertiary, and some is much earlier.

*Influence of Earth Sciences on Mineral Development.* A broad knowledge of the geology, physiography, and history of California is essential in the discovery, development, and utilization of the mineral resources of the state. Even future economic trends can be predicted with greater success, if these features are carefully and continually studied and the facts scientifically weighed and placed in systematic order. For these reasons, the Division of Mines has embarked on extensive statewide studies of the geology of mineral deposits.

#### POSITION OF MINERAL DEPOSITS IN TYPICAL STRATIGRAPHIC SECTIONS OF CALIFORNIA

Throughout the discussions of mineral commodities described in this volume, frequent reference is made to the geologic age or geologic formation in which the mineral deposit is found. In the following typical stratigraphic sections, selected from various parts of the state, are indicated the positions occupied by mineral deposits. In many cases the mineral deposit was formed at the same time or as a part of the geologic formation. In other cases the mineral body was deposited in the formation, but at a later time. In the study and search for mineral deposits, this information is of considerable importance for it may lead to a better understanding of the environment which was particularly favorable to deposition.

Locations of the numbered stratigraphic sections may be found on the accompanying map of California.

#### Typical Stratigraphic Sections

##### (1) Northern Klamath Mountains

(after F. F. Cater and F. G. Wells, 1953)

AGE	FORMATION	MINERAL DEPOSIT
Quaternary	Alluvium	Placer gold, platinum
Miocene (?)	Gravel deposits	Placer gold
Upper Jurassic or Lower Cretaceous	Granitic rocks	Gold lode, quicksilver
	Serpentine-peridotite	Chromite (largest producers in U. S.), asbestos, copper, quicksilver.
Upper Jurassic	Galice Dothan	Manganese Gold lode

##### (2) Redding Region

(after J. S. Diller, 1906, and N. E. A. Hinds, 1933)

AGE	FORMATION	MINERAL DEPOSIT
Quaternary	Red Bluff gravels and alluvium	Placer gold
Pliocene	Tehama	
	Tuscan	Building stone
Eocene-Palocene	Weaverville	Placer gold, lignite
	Montgomery Creek	Lignite
Cretaceous	Chico	Building stone
	Shasta series	
	Knoxville	
	Serpentine	Chromite
Jurassic	Granitic intrusive rocks	Gold
	Potom Bagley andesite Modin	
	Brock shale	
	Hosselkus limestone	Limestone
Triassic	Pit Bully Hill rhyolite	East Shasta copper-zinc district, lead, gold, silver.
	Dekkas andesite	
Permian	Nosoni	Iron
	McCloud limestone	Limestone, iron
Mississippian	Baird Bragdon Bass Mt. basalt	
Devonian	Kennett	Limestone
	Balaklala rhyolite	West Shasta copper-zinc district, silver, gold
Devonian or older	Copley Chanchehulla Salmon schist Abrams schist	

##### (3) Warner Range

(modified after R. J. Russell, 1928)

AGE	FORMATION	MINERAL DEPOSIT
Recent to Pliocene	Obsidian Rhyolite	Perlite
Pliocene	Warner basalt	
Miocene	Upper Cedarville	Pumice
	Middle lava layer Lower Cedarville	



(4) *Northern Coast Ranges*  
(after E. H. Bailey, 1946)

AGE	FORMATION	MINERAL DEPOSIT
Quaternary	Alluvium Basalt	
Tertiary	Silica-carbonate rock	Quicksilver
	Sonoma volcanics	Perlite, pumice, building stone
Jurassic (?)	Gabbro and diorite	
	Knoxville Serpentine Franciscan group	Quicksilver Quicksilver, chromite Quicksilver, manganese

(5) *West Side Sacramento Valley*  
(modified after Am. Assoc. Petroleum Geologists Correlations Committee, 1951, 1954)

AGE	FORMATION	MINERAL DEPOSIT
Quaternary	Alluvium	Placer gold
	Red Bluff gravels	Placer gold
Pliocene	Tehama	Gas (Corning field)**
Miocene	San Pablo group: Neroly Cierbo	
	Markley Nortonville	
Eocene	Domengine	Gas (Rio Vista field), coal (Mt. Diablo)
	Capay Meganos	
Paleocene	Martinez	
Upper Cretaceous	"Chico"	Gas (several Sacramento Valley fields)
Lower Cretaceous	Horsetown group Paskenta	
Jurassic	Knoxville	Quicksilver*
	Franciscan	Quicksilver*

\* Age of mineralization much later than age of host formation.

\*\* Tehama formation serves only as the reservoir rock for the gas.

(6) *Alleghany Area*  
(modified after H. G. Ferguson and R. W. Gannett, 1932)

AGE	FORMATION	MINERAL DEPOSIT
Quaternary	Stream gravel Basalt	Placer gold
Tertiary	Andesite breccia	
Eocene	Auriferous gravel	Placer gold
Upper Jurassic (?)	Granitic intrusives	
Jurassic to Paleozoic	Gabbro, diorite Serpentine Amphibolite schist Diabase	Lode gold quartz veins (a major source of lode gold in California)
Permian to Carboniferous	Delhi Cape Horn slate Relief quartzite Kanaka Tightner Blue Canyon	

(7) *Sierran Foothill Area*  
(composite section after N. L. Taliaferro, 1943, 1946)

AGE	FORMATION	MINERAL DEPOSIT
Quaternary	Alluvium Terraces	Placer gold
Pliocene or Pleistocene	Table Mt. latite	
Pliocene	Mehrten (andesitic)	
Upper Miocene	Valley Springs (rhyolitic)	Building stone (tuff)
Eocene to Pleistocene	Channel deposits	Placer gold
Eocene	Ione	Clay, lignite, quartz sand
Upper Jurassic	Intrusive granitic rocks	Lode gold, copper
	Serpentine—ultramafic rocks	Chromite, asbestos, copper, magnesite, iron
	Silica-carbonate rock	
	Mariposa	Lode gold
	Quartz porphyry	
Carboniferous (?)	Logtown Ridge	Chromite, manganese, lode gold, silver, copper-zinc
	Cosumnes	Manganese
	Calaveras group	Limestone, iron, gold



8) *Mather Lode Area*  
(after A. Knopf, 1929)

AGE	FORMATION	MINERAL DEPOSIT
Quaternary	Alluvium and river gravel	Placer gold
Tertiary	Volcanic flows and tuffs Auriferous gravel	Building stone Placer gold
Jurassic or Cretaceous	Granitic rocks Serpentine	Lode gold Lode gold, asbestos, chromite
Upper Jurassic	Mariposa	Lode gold (largest producing mines)
Carboniferous-Jurassic	Metavolcanic rocks	
Mississippian	Calaveras	Limestone, lode gold

9) *Central Coast Ranges (Santa Cruz-Gabilan Ranges)*  
(after J. E. Allen, 1946)

AGE	FORMATION	MINERAL DEPOSIT
Recent	Alluvium	Sand and gravel
Pleistocene	Aromas red sands	
Pliocene	Purisima	
Upper and middle Miocene	Monterey group Volcanic group	Oil (Sargent oil field)
Lower Miocene	Vaqueros	
Oligocene	San Lorenzo	Oil (Moody Gulch oil field)
Upper Jurassic	Serpentine	Chromite
	Franciscan group	Quicksilver, manganese, magnesite
Pre-Franciscan	Santa Lucia	Crushed rock
	Gabilan limestone	Limestone, dolomite, barite

(10) *West Side San Joaquin Valley*  
(after R. S. Beck, 1950, unpublished and others)

AGE	FORMATION	MINERAL DEPOSIT
Pleistocene	Tulare	Gypsite
Pliocene	San Joaquin clay Etchegoin	
Plio-Miocene	Reef Ridge shale	
Miocene	Upper McLure, Antelope and McDonald shales	
	Middle Devilwater-Gould shale	
	Lower Temblor	
Oligocene	Wagon Wheel Tumey	
Eocene	Kreyenhagen Avenal sandstone Yokut	
	Arroyo Hondo shale Cantua sand	
	Cerros and Martinez	
Paleocene	Dos Palos Cima sand	
Upper Cretaceous	Moreno shale Panoche	
Upper Jurassic (?)	Franciscan group	Quicksilver

(11) *East Side Southern Sierra Nevada*  
(after A. Knopf, 1918, and P. C. Bateman, 1954)

AGE	FORMATION	MINERAL DEPOSIT
Recent	Alluvium	Placer gold
Pleistocene and Recent	Fan deposits	
	Basalt flows and cinders	Volcanic cinders
Pleistocene	Glacial deposits	
	Rhyolite flows and tuffs	Perlite
Cretaceous (?)	Granitic intrusives	Feldspar, gold lode
Triassic	Metavolcanic rocks	
Paleozoic (?) and Triassic (?)	Metasedimentary rocks of Sierra Nevada	Tungsten, talc.



(12) *Southern Inyo Range*  
(after J. F. McAllister, 1955)

AGE	FORMATION	MINERAL DEPOSIT
Quaternary and late Tertiary (?)	Alluvium, fanglomerate, lake beds, basalt	Placer gold, salines, fuller's earth, perlite
Cretaceous (?)	Granitic rocks	Lead-zinc-silver, gold lode
Permian	Bird Spring (?)	Lead-zinc-silver
Carboniferous	Rest Spring shale	
	Perdido	Lead-zinc-silver
	Tin Mountain limestone	
Devonian	Lost Burro	Lead-zinc-silver, copper, gold
Silurian	Hidden Valley dolomite	Building stone, roofing granules
Ordovician	Ely Springs dolomite	Talc, copper, lead-zinc-silver
	Eureka quartzite	Talc, quartzite
	Pogonip limestone	Talc, copper
Cambrian	Nopah limestone Racetrack dolomite	

(13) *Death Valley Area*  
(after J. F. Mason, 1948)

AGE	FORMATION	MINERAL DEPOSIT
Quaternary	Alluvium	
	Lake beds	Pumicite, bentonite
	Basalt flows	
Tertiary	Volcanics and lake beds	Borax, perlite, gypsum, salt
Carboniferous	Monte Cristo limestone	Limestone
Cambrian	Cornfield Springs Bonanza King Cadiz Wood Canyon Stirling quartzite Johnnie	
	Noonday dolomite	Lead-silver-zinc
Pre-Cambrian	Algonkian Kingston Peak Beck Spring	
	Cryetal Spring	Talc, iron
	Archean Granite gneiss	Gold lode, rare earth minerals.

(14) *Southern Sierra Nevada and San Joaquin Valley*  
(after Dibblee, 1955)

AGE	FORMATION	MINERAL DEPOSIT
Quaternary	Alluvium	Placer gold
Plio-Pleistocene	Kern River	Oil and gas*
	Tulare	
Mio-Pliocene	Chanac	Oil and gas*
	Bena	
Miocene	Santa Margarita Maricopa Round Mountain silt Olcese sandstone Temblor Freeman shale Pyramid Hilla sand Vedder sand	Major oil and gas fields
Oligocene (?)	Walker	Oil and gas
	Bealville fanglomerate	
	Tecuya	Oil and gas†
Eocene	Tejon	Oil and gas
Jurassic (?)	Granitic intrusions	Gold-silver quartz veins, uranium
Paleozoic-Triassic (?)	Kernville schist	Gold lode
	Pampa achist	
	Limestone	Limestone
Pre-Cambrian (?)	Pelona schist	Building stone Soapstone

\* These continental sediments serve as reservoir rock only. Oil originated in older marine sedimentary formations.

† Tecuya continental sediments serve as reservoir rock, while marine strata may be the oil source rocks.



15) *Western Santa Ynez Mountains*  
(after T. W. Dibblee, 1950)

AGE	FORMATION	MINERAL DEPOSIT
Recent	Alluvium	
Pliocene	Sisquoe	Oil and gas Diatomite
Miocene	Monterey	Oil and gas
	Tranquillon	
	Rincon Vaqueros	Oil and gas Oil and gas
Oligocene	Sespe	
	Alegria	Oil and gas*
	Gaviota	
Eocene	Sacate	Oil and gas
	Cozy Dell Matilija Anita Sierra Blanca	Limestone
Cretaceous	Jalama Espada	
Upper Jurassic	Honda Serpentine	
	Franciscan	Manganese, quicksilver

\* Nonmarine Sespe beds serve as reservoir rock; oil may have originated in younger or older formations.

16) *Los Angeles Basin*  
(composite section after J. E. Schoellhamer, J. G. Vedder,  
and R. F. Yerkes, 1954)

AGE	FORMATION	MINERAL DEPOSIT
Recent	Alluvium	Sand and gravel aggregate, clays
Pleistocene	La Habra	Shallow oil production
Pliocene	Pico Repetto	Major oil and gas fields
Upper and middle Miocene	Puente-Modelo-Monterey	Palos Verdes diatomite Major oil and gas fields
Middle Miocene	Topanga	Oil and gas
Lower Miocene— Upper Eocene	Vaqueros-Sespe	
Middle Eocene	Santiago	Lignite
Paleocene	Silverado, Martinez	Lignite
Upper Cretaceous	Williams Ladd Trabuco	} "Chico" Building stone
Jurassic	Santiago Peak volcanics	
	Granite	Crushed rock, gold quartz veins
Triassic	Bedford Canyon	
Triassic (?)	Santa Monica slate	
Mesozoic or older	Catalina schist	Oil from fractured schist* Lead-silver-zinc (Santa Catalina Island)

\* Fractured schist serves as the reservoir rock, while oil originated in rocks of much younger age.

17) *Barstow Area*  
(after O. E. Bowen, 1952)

AGE	FORMATION	MINERAL DEPOSIT
Pleistocene	Alluvium	Placer gold, marl, filler
Pliocene	Rhyolite flows and plugs	Silver-barite, gold-quartz veins
Miocene (?)	Volcanics and lake beds	Silver-barite veins, magnesite
Jurassic (?)	Granitic intrusions	Lead-zinc-silver, gold-quartz veins
Triassic (?)	Sidewinder volcanic series	Gold-silver quartz veins, filler clay, pyrophyllite, copper, iron.
Permian	Fairview Valley	Limestone
Carboniferous	Oro Grande series	Gold-silver, limestone, dolo- mite, magnesite, silica, copper.
Paleozoic (?)	Waterman gneiss	
	Hodge volcanic series	Filler, clay, silica
	Granite gneiss	

18) *Julian District*  
(modified after D. L. Everhart, 1951)

AGE	FORMATION	MINERAL DEPOSIT
Quaternary	Alluvium	Placer gold
Cretaceous	Quartz veins, dikes, pegma- tites	Feldspar, silica
	Granite	
	Cuyamaca gabbro	Nickel, building stone
Jurassic (?)	Stonewall granodiorite	Gold-quartz veins
Triassic (?)	Julian schist	Gold-quartz veins







MINERAL  
COMMODITIES







## ABRASIVES

BY BENNIE W. TROXEL

Abrasives are substances that are used to grind, polish, scour, or clean by abrasion or impact. They include naturally occurring minerals and manufactured substances made from metals or mineral raw materials. Sand, pumice, and pumicite are the principal abrasives produced in California. Garnet, talc, diatomite, and pebbles for grinding are also obtained from sources in the state, and are used as abrasives but in small quantities. Garnet, artificial abrasives, corundum, diamonds, and grinding pebbles from out-of-state sources, constitute most of the high-quality abrasives used in California.

### ABRASIVES AS CLASSIFIED BY USE

The physical properties that determine the usefulness of an abrasive material are hardness, toughness, grain shape and size, purity, uniformity, and the character of fracture or cleavage. Nearly all abrasive grains must break down slowly under use to furnish fresh cutting edges.

**Loose Grains.** A wide variety of mineral abrasives are employed in the form of loose grains, such as those used as impact abrasives or as constituents of dentifrices, cleansers and polishes. Of the impact abrasive materials, silica sand is the most abundant and most widely used (see section on sands elsewhere in this volume), and garnet ranks second in quantity consumed. Uniform-sized grains, tough enough to withstand disintegration under impact, and having a specific gravity and hardness at least as great as quartz are generally specified for impact abrasives.

Loose grains of sand, garnet, emery, corundum, pumice, diatomite, metallic oxides, manufactured carbides, and diamond dust are utilized to abrade stone, glass, gems, metals, plastics and wood. The abrasive agents used in scouring soaps, cleansers, and abrasive polishes are mostly fine-ground natural materials such as feldspar, pumice, pumicite, sand, quartz, diatomite and clay. Household cleansers contain abrasives that are somewhat softer than glass and of uniform hardness. They should not contain harder impurities nor lime compounds that react with soaps to form insoluble residue on surfaces being cleaned. Pumice, pumicite, diatomite, and probably clay, all mined in California, are used in these products.

**Bonded Abrasives.** Bonded and pressed or molded abrasive products, containing either natural or artificial abrasive grains, are used in a wide variety of forms. Nearly all bonded abrasives are electric furnace products, principally aluminum oxide or silicon carbide, but natural corundum is still employed in this manner.

Bonded abrasive products consist mostly of grinding wheels, but they also are formed into rectilinear and curved blocks, and into segments of curved blocks. In such products the abrasive grains must withstand high bonding temperatures and must be well-suited to the binder. Bonded abrasive products are used extensively in California but the artificial abrasives that they contain are manufactured elsewhere.

**Coated Abrasives.** Coated abrasives consist of crushed and closely sized abrasive grains cemented to paper or cloth backing. Such abrasives must unite well with the

binder. The products are generally known as sandpaper, emery cloth or garnet paper. The principal abrasives used for this purpose are crushed quartz, garnet, aluminum oxide, and silicon carbide. Easily cleavable, brittle, or friable grains generally are not satisfactory for coated abrasives because they break down too rapidly, nor are extremely tough grains desirable because new cutting edges do not form readily and the useful life is shortened. The abrasive papers and cloths are widely utilized in hand and machine finishing and preparation of wood, metal and plastic surfaces. Coated abrasive products are supplied mainly from plants in New York State.

**Products Shaped From Natural Stone.** Grindstones, pulpstones, millstones, chaser stones, and sharpening stones, which were formerly made from shaped natural rocks, including sandstone, quartzite, granite, quartz conglomerate, mica schist, siliceous argillite, shale, slate, pumice, novaculite, and phyllite have been replaced largely by products composed of artificial abrasives made in the electric furnace. Pumice quarried from deposits in Mono and Siskiyou Counties is the only natural material in California that is marketed as a shaped abrasive product.

### NATURAL ABRASIVES

**Garnet.** The specific name "garnet" is applied to a mineral group composed of six closely related sub-species: almandite,  $\text{Fe}_3\text{Al}_2(\text{SiO}_4)_3$ ; andradite,  $\text{Ca}_3\text{Fe}_2(\text{SiO}_4)_3$ ; grossularite,  $\text{Ca}_3\text{Al}_2(\text{SiO}_4)_3$ ; pyrope,  $\text{Mg}_3\text{Al}_2(\text{SiO}_4)_3$ ; spessartite,  $\text{Mn}_3\text{Al}_2(\text{SiO}_4)_3$ ; and uvarovite,  $\text{Ca}_3\text{Cr}_2(\text{SiO}_4)_3$ . Garnet crystallizes in the isometric system, but is commonly granular or massive. It ranges in hardness from 6.5 to 7.5 and has a specific gravity range from 3.5 to 4.2. Garnet crystals are generally tougher than granular varieties or massive garnet which are commonly friable. Garnet has a vitreous to resinous luster and occurs in various colors, mostly red, brown or yellow.

Garnet occurs in a wide range of geologic environments. Of greatest commercial interest as abrasives are almandite, which occurs in schists and gneisses, and andradite, which occurs in contact metamorphosed limestone, schist, serpentine, and some igneous rocks. Gem garnet is discussed in the section on gem stones in this volume.

For use in coated abrasive products, garnet should be about 7.5 in effective hardness and should break into sharp, angular fragments when crushed. Tough grains, brittle enough to yield new cutting edges under the strain of work, are preferred. The grains should break into angular fragments of somewhat regular shape, not slivers or thin particles, and should be free of embedded impurities. The crushed garnet should have a high capillary attraction to binders. The color of garnet apparently is independent of its abrasive qualities, but deep red or wine colors are preferred by consumers. For maximum yield of desired sizes during crushing, garnet grains should be the size of peas or larger. Smaller sizes usually yield a high proportion of fines which is undesirable.

Garnet for impact abrasives must be tough, of high specific gravity, of uniform size, dust free, and nearly



pure. It is used in sizes between 17 mesh and 45 mesh. Garnet that shatters easily upon impact has very little abrasive effect. Garnet is a more efficient impact abrasive than silica sand because it is tougher and has a higher specific gravity. Although it costs several times as much as silica sand, it can be reused as many as 10 or more times, depending on original grain size, toughness, air pressure, and other variable factors. Most of the abrasive garnet that has been recovered in California has been used only once.

The toughness of garnet can be crudely tested by placing a small amount of the clean raw material between two iron or steel plates and striking them with a hammer. Tough garnet will yield chips, whereas soft or brittle garnet will yield fine powder or dust. Trial by actual use is the best test.

The first use of garnet on coated paper was in 1880. For a short period prior to that time, carnelian, a variety of chalcedony, was mined in California, shipped to New York, and used as an abrasive paper known as ruby paper. The supplies of carnelian from California were limited, delivery uncertain, and eventually its use was abandoned (Myers and Anderson, 1925, p. 12).

Most of the garnet mined in the United States is obtained from the property of the Barton Mines Corporation at Gore Mountain, Warren County, New York. This property has been in continuous operation for over 75 years (Chandler, 1956, p. 296) and still contains large reserves of garnet. The garnet-bearing rock is massive and granular and is composed principally of hornblende and feldspar. It contains an average of 10 to 12 percent of almandine garnet which occurs as large, imperfectly developed crystals (Myers and Anderson, 1925, pp. 18-19). The crystals commonly exceed one foot in diameter, and some are as much as 36 inches in diameter. Most of the crystals are surrounded by thin shells of hornblende. The principal deposit is about  $\frac{3}{4}$  mile long, from 50 to 300 feet wide, and extends to an undetermined depth. It is mined in an open cut and the operation is fully mechanized (Chandler, 1956, p. 296). The rock is milled by means of a heavy-medium separation process. Garnet also is derived as a by-product from an extensive deposit of wollastonite near Willsboro, New York, being mined by Godfrey L. Cabot, Incorporated.

New York garnet has become widely used, as it exists in large quantities, is of excellent abrasive quality, and the deposits are near the principal markets (Chandler, 1956, p. 296). It is referred to as "Adirondack garnet" and nearly all of it is used in coated abrasives.

In Idaho, extensive alluvial deposits that contain almandite garnet derived from erosion of soft mica schists, are mined by Idaho Garnet Abrasive, Fernwood, Idaho. The deposits are on Emerald Creek in Benewah County, Idaho. Garnet comprises as much as 20 percent of the mined material, and its maximum grain size is about  $\frac{3}{16}$  inch (Chandler, 1956, p. 296). Mining is conducted by dragline after an overburden of 3 to 8 feet is removed. A 99 percent garnet concentrate is obtained by means of jigs and concentrating tables. This is dried, crushed, and screened into various sizes (Chandler, 1956, p. 296). Idaho garnet is used principally as an impact abrasive and a large proportion of the output is consumed in California. Garnet also is recovered as a by-product from extensive placer concentrations of monazite-rutile-ilmenite-bearing sands in Florida.

In California, garnet is a common mineral, but relatively little is known about the abrasive qualities of the material in most deposits. Grossularite is abundant in impure limestone bodies that have been metamorphosed near contacts with intrusive igneous rocks. This is also the geologic environment of most of the tungsten deposits in the state. These metamorphosed rocks, commonly called tactite, skarn, or lime-silicate rocks, are found in many parts of the Sierra Nevada, Mojave Desert, Colorado Desert and the Peninsular Ranges. Garnet in contact zones occurs as disseminated crystals, as aggregates of crystals, granular masses, and massive layers of nearly pure garnet, as much as two or more feet thick and several tens of feet long. Some contact zones consist of more than one-half garnet and extend over areas many tens of feet wide and hundreds of feet long.

Since 1938, Huntley Industrial Minerals, Inc., and others, have intermittently produced small tonnages of garnet, principally grossularite, from tungsten mill tailings in Inyo County. The concentrates have been marketed as impact abrasives and used mostly by the aircraft industry. Some garnet from the Bishop area is reported to have been utilized for cleaning military equipment. Because most of the tungsten ore is ground to minus 12 mesh or smaller in these mills, the garnet is generally too fine to be useful as an impact abrasive.

In several parts of the state, principally in the Sierra Nevada and in the northern Coast Ranges, gneisses and schists contain almandite and/or andradite in evenly disseminated crystals which generally are one-eighth inch or less in diameter. Locally they are several inches in diameter. A deposit of andradite garnet northwest of Cadiz, San Bernardino County, was prospected in 1931-1932 and a few tons of garnet rock were mined at the Sunny Day mine near Indio, Riverside County, in 1936-1937 but no shipments were made (Eardley-Wilmot, 1937, p. 23).

Uvarovite, which is much less common than grossularite, is a minor constituent of chromite deposits in the Klamath Mountains, the Sierra Nevada, and the Coast Ranges. Eclogite, a medium-grained granulose rock composed of almandite garnet and pyroxene, has been found locally in northern California. This rock is a possible source of abrasive garnet, but nearly all known outcrops are small. Some of the pegmatite bodies of southern California contain gem garnet (see gem section in this volume), but are not rich enough in ordinary garnet to supply abrasive markets. Rarely do other igneous rocks contain garnets that are larger than pin heads and that comprise more than one percent of the rock.

Garnet derived from igneous and metamorphic rocks is common in heavy mineral concentrations of placer sands. Such deposits, commonly known as black sands, are distributed along much of the coast of California and in placer deposits along the western side of the Sierra Nevada (see section on black sands in this volume). The garnet in these sands is generally too small for use as impact abrasives and, in most concentrations, is so well rounded that it would have to be crushed to provide sharp cutting edges. It might, however, be useful as fine-ground garnet for polishing compounds if a large enough market were developed.

Most of the loose-grain garnet consumed in California is used as impact abrasives, principally by the aircraft



industry and other fabricators of non-ferrous metal products. Large quantities of garnet-coated abrasives also are consumed in the state. For impact abrasion, garnet is employed much less abundantly than silica sand. Largely because garnet is the more expensive, its use is ordinarily restricted to the scouring and abrading of non-ferrous metals. In 1955, probably 7,000 to 10,000 tons of concentrates, containing 98 percent or more of dust-free garnet from Idaho, was consumed in California. Idaho garnet was marketed in the size range of 17 mesh to 45 mesh at a price of about \$100 per ton delivered in Los Angeles. Only a few tens of tons of Adirondack garnet, in fine-ground sizes between 325 mesh and a theoretical 3600 mesh, is marketed per year in California for use in polishing optical glass and similar material. During 1955, this material sold for about 35 cents to 51 cents per pound in 50 pound lots delivered in California. California garnet that is used as an impact abrasive is sold in the range of \$8 to \$12 per ton, f.o.b. mine. Probably less than 100 tons were marketed in 1955. In California no market exists for garnet for use on coated abrasive products as these are manufactured in the eastern United States near the sources of supply.

Persons desiring to market garnet for abrasives must ordinarily be prepared to furnish a clean, pure, dust-free product, ready ground and sized for use. Most purchasers prefer to obtain material from established suppliers of abrasive products, many of whom are interested in obtaining abrasive material from local sources.

*Pumice and Pumicite.* (See also section on pumice, pumicite, perlite, and volcanic cinders in this volume.) Pumice and pumicite are desirable abrasive materials principally because they are among the few coherent moderately soft rocks composed wholly of one substance and hence of uniform hardness. Of the 70,964 tons of pumice and pumicite mined in California in 1954, probably only 5 to 10 percent was used for abrasive products; the remainder was used mostly as aggregate, filler material, and pozzolan. The pumice and pumicite that are used for abrasives ordinarily command higher prices than the pumice and pumicite that are employed otherwise, but the abrasive market is limited and, at present, is supplied by operators whose principal markets are for non-abrasive products. In California, no pumicite operations are being conducted solely as sources of abrasive material, although the output of block pumice quarries in Mono and Siskiyou Counties is used almost entirely in the manufacture of shaped abrasive blocks. These quarries supply nearly all of the demand for scouring blocks in the United States.

Pumice and pumicite are glassy and cellular, light-colored rocks, generally rhyolitic in composition, which have been expelled from volcanic vents. Pumice forms as the glass congeals around expanding gas and steam bubbles to yield silky, glass fibers or elongated and rounded cells ranging in size from microscopic to several inches in diameter. The cell openings ordinarily comprise about two-thirds of the volume of the rock. Pumice ranges in specific gravity from about 2.5 for nonporous volcanic glass to less than 1 for extremely cellular material. Pumicite, also called volcanic ash, is of finer grain size. Much of the naturally occurring pumicite and is distinguished from pumice solely on the basis of grain size. Much of the naturally occurring pumicite

ranges in size from 100 to 325 mesh. Some occurrences of pumice and pumicite are extremely pure, but others commonly contain various proportions of other materials, especially sand, silt, or clay.

In an industrial sense, the term "block pumice" is applied to crude pumice that occurs in blocks large and strong enough to be sawed or shaped to desired forms. Lump pumice refers to small fragments, either ground, shaped, or in the natural state.

Pumice and pumicite are abundant in the terranes of Tertiary to Recent volcanism that cover large areas throughout California. They also occur in sedimentary rocks far removed from such regions. They have been mined mostly in Inyo, Mono, Napa, Siskiyou and Stanislaus Counties. Seven of the operations in these counties have yielded most of the pumice and pumicite that has been mined in California for abrasive use, but several other properties also have contributed small quantities. These localities are described in the sections on pumice and pumicite, perlite, and volcanic cinders elsewhere in this volume.

Pumice blocks suitable for cutting into scouring blocks are mined by U. S. Pumice and Supply Co., Inc., in the Glass Mountain area, Siskiyou County, and near Lee Vining, Mono County (Chesterman and Schmidt, 1956). Occurrences of mineable block pumice of this quality are rare in the United States.

Volcanic ash (pumicite) and pumice in the Pliocene Ricardo formation have been mined from four properties in the Last Chance Canyon area of El Paso Mountains, Kern County (Dibblee and Gay, 1952, pp. 50-53). Calsileo Corporation, with offices in Los Angeles, supplies ground material for abrasive markets from one of the largest of these deposits.

Pumicite for abrasives has been mined from flat-lying Pleistocene lake beds in Amargosa Valley near Shoshone, Inyo County (Norman and Stewart, 1951, p. 109), and pumice and pumicite have been mined from deposits near Friant on both sides of the San Joaquin River in Fresno and Madera Counties (Chesterman and Schmidt, 1956). Several properties in Mono County have yielded pumice for abrasives (Chesterman and Schmidt, 1956), and an indurated white volcanic ash in San Luis Obispo County was mined for abrasive material (Franke, 1935, pp. 460-461).

Pumice and pumicite are effective as abrasives yet do not scratch the surfaces of most metals, glass, or porcelain. Block pumice is particularly adaptable for the manufacturing of scouring blocks which are used to clean cooking griddles, utensils, and similar items.

Most lump pumice is used, in the form of small, fabricated blocks, for hand rubbing of glass and stone, cleaning stone surfaces of lithographing plates, rubbing down finished steel and wood surfaces as well as painted surfaces, finishing leather, preparing surfaces for silver plating, and in the electroplating industry for cleaning buffing wheels. Some of the highest grade lump pumice is used as a toilet article to remove, by abrasion, cuticles, calluses, and stains on the skin. Pumice in sizes from sand grains to peas is used as an abrasive in tumbling barrels to deburr moderately soft metal products.

Fine-sized (minus 100 mesh or smaller) pumice is used in compounds for finishing and polishing silverware, jewelry, and other metalware; finishing auto bodies; glass cutting and beveling; finishing fine wood surfaces;



and rough rubbing. It also is used in household cleansing compounds and soaps, rubber erasers, and for abrading and finishing hard rubber and fiber board. Very fine-sized, air-floated ground pumice and pumicite are used for precise abrasive work and in dental powder and paste.

Pumice for scouring blocks and lump pumice should be free of hard ribs of unexpanded glass and crystals of quartz and feldspar, and should consist of lumps from which useful sizes can be trimmed. Cell openings should be uniform in size and evenly spaced, so that the rock has a uniform hardness, strength, and will wear evenly. The rock should be tough enough to withstand disintegration during use.

Pumicite mined for other uses can be used in abrasives if it is relatively free of sharp, gritty, particles of silica or other hard substances that scratch and from alteration products such as bentonite. The removal of excessive quantities of impurities from pumicite may be prohibitively expensive. Pumicite or ground pumicite for use in cleansers should be white, both when wet or dry. Impurities that cause alkaline reactions with soap are undesirable.

For fine-grained polishing compounds, pumice or pumicite should consist of thin, curved, uniformly sized fragments or particles of hollow, silky fibers. Such materials probably scratch less than those composed of angular or thick particles.

Crude pumice and pumicite for the abrasive market are dry ground and screened with standard mechanical equipment, and then dried and bagged for shipment. Unexpanded glass, phenocrysts of quartz, feldspar, or mica, or alteration products such as clay, must be removed to yield high-quality abrasive material. As most of these impurities are heavier than pumice and pumicite, they can be separated on dry concentrating tables or screens. Fine grinding, if necessary, is accomplished by wet methods. Extremely small sizes are obtained by air separation of finely ground material.

Ground pumice and pumicite are classified and bagged in 11 or more sizes which range from very fine air-floated powder (grade FFFF) to sand or pea-sized material. Block pumice is usually hand sorted to obtain suitable material and is then sawed to rough or finished shapes. Lump pumice is marketed into at least 7 sizes ranging from small lumps to lumps 7 or more inches in diameter.

Tests and specifications for abrasive pumice and pumicite are not standardized and vary according to the type of end product desired. Most abrasive consumers perform their own tests, principally by trial, and set their own specifications. Expanded perlite, a pumice that is manufactured by rapidly expanding natural perlite in a furnace, is competitive with natural pumice abrasives. Certain types of expanded perlite are superior to natural pumice for some abrasives, because the expanded perlite can be made more uniform in all physical properties and is snow white both wet and dry (King, 1948, p. 297).

Pumice and pumicite for abrasive use are usually marketed in specified sizes to wholesale jobbers or directly to the consumer. Material from some deposits is mined, processed, and converted to abrasive products by a single firm.

Ground and lump Italian pumice are competitive with local material and the market is so limited that most

California producers do not attempt to market material for abrasive use. In California, no operators who produce fine-ground or lump pumice market them exclusively as abrasives, but supply other markets as well. Some California material is marketed outside the state. Markets in other western states are supplied principally from sources within those states or from Italian sources, and markets in the eastern United States are supplied mainly from Italian sources.

The pumice and pumicite deposits that are nearest to industrial centers and that can be mined and processed most inexpensively are in the best competitive position. Deposits should be readily accessible, and should be free of excessive overburden. As the pumice that is suitable for cutting into blocks has a higher unit value than other pumice, it can be quarried at greater distances from markets.

The following prices are quoted from the Oil, Paint and Drug Reporter, May 1956. Pumice, domestic, ground coarse to fine sizes (minus 100 to minus 30 mesh), bagged, in ton lots, 4½ cents per pound. Imported Italian, silk screen, coarse, bagged, in ton lots, 6½ cents per pound; fine, 4 cents per pound.

In 1956 ground pumicite from El Paso Range, Kern County, ranged in price from \$45 per ton for minus 9 mesh to \$70 per ton for 400 mesh, f.o.b. mine. Retail prices for abrasive articles made from block pumice ranged from 15 cents for blocks 1½ by 1½ by ¾ inches to \$1.00 for 4 by 4 by 8 inch scouring blocks.

**Corundum.** Corundum ( $Al_2O_3$ ), the second hardest mineral known, was once an important abrasive material but its use has been largely supplanted by the artificial abrasives silicon carbide and fused aluminous oxide.

Corundum has a hardness of 9, is brittle to tough, and generally occurs in silica-poor metamorphic or igneous rocks. The best known deposits are in Canada, India, Union of South Africa, Madagascar, and the United States. It comprises as much as 75 percent of the rock in which it occurs, but generally is much less abundant. The corundum-bearing rock mined in Canada has averaged 10 percent or less. Corundum also has been mined from alluvial deposits, especially in Africa and India.

Occurrences of corundum are uncommon in California, and those that are known have not been considered to be of commercial importance. Most of these occurrences are in metamorphic and igneous rocks in Los Angeles, Mono, Plumas, Riverside, and San Bernardino Counties. Corundum in gravels has been reported in Butte and Los Angeles Counties (Murdoch and Webl, 1948, p. 122).

Corundum has been used principally in grinding wheels, in polishing compounds, as coated abrasives, and in sharpening stones. Although its use has been sharply curtailed since the advent of artificial abrasives, corundum is still employed to a limited extent.

Corundum for use as an abrasive should be pure and tough, and when broken under pressure, should furnish new cutting edges. Fine-grained material is not salable because it yields a high percent of dust. Most buyers judge first by general appearance and, if satisfactory, the material is made into finished products and tested by actual use.

In 1956, crude corundum was quoted at \$100 to \$120 per ton c.i.f. U. S. ports (Eng. and Min. Jour. Min. Me



Markets). In the United States, the American Abrasive Company of Westfield, Massachusetts, was the only firm that was importing and concentrating corundum in 1955 (Chandler, 1956, p. 248). Natural crystal corundum is on the national stockpile list; specifications are obtainable from U. S. General Services Administration, Emergency Procurement Service, Washington 25, D. C.

**Industrial Diamonds.** Although diamonds are not produced commercially in California, large numbers of industrial diamonds are consumed annually in the state. Their use as abrasives has increased in spite of a steady increase in price since World War II.

Diamond, a crystalline form of carbon, is the hardest substance known. It is valued as a gem and is the most effective of the abrasive materials. It occurs in pipes of serpentinized ultrabasic rocks (kimberlite) and is concentrated in placer deposits. Nearly all of the world supply of diamonds is obtained from deposits in Africa and South America. Impure, granular to crystalline, off-color or flawed diamonds are used as abrasives and are known commercially as "bort," "carbonado" and "ballas."

Placer deposits in California have yielded an estimated 500 to 600 diamonds since 1849 (Murdoch and Webb, 1948, pp. 130-131). Most of these stones were found when placer mining for gold was most active. The stones are small and tinted yellow, but a few of them weigh more than 2 carats and are nearly clear. Nowhere in California have diamonds proved abundant enough to be mined commercially (see section on gem stones in this volume).

An estimated 50,000 to 70,000 carats of industrial diamond (bort) is consumed each month in California. Probably most of this is in the crushed or fragmented form, and some is in powder form. The diamonds are mounted on edges of circular saw blades which are used to cut expansion joints in green concrete, to cut openings in mature concrete, and to trim such materials as tile, stone, glass, and semi-precious stones. They also are mounted in drill bits for oil well drilling and mineral exploration. Grinding wheels containing diamonds are used for sharpening and trimming cemented carbide tools and wheels. Diamonds are utilized also in wire-drawing dies, and finely ground diamond is used as a polishing and lapping agent.

The value of industrial diamonds imported for consumption in the United States in 1953 averaged \$3.67 per carat (Chandler, 1956, p. 256). This value does not include manufactured bort (diamond dies) and diamond dust. Prices vary considerably depending on the quality and size of the diamond.

**Sand.** In 1952, about 121,000 tons of sand from California was marketed for use as an impact abrasive (sandblasting). Most of the sand is obtained from natural dunes and beach deposits that border Monterey Bay, and from the beaches of southern California, notably the El Segundo area (see section on special sands in this volume).

**Quartz, Quartzite and Sandstone.** Quartz, quartzite, and sandstone may be ground and graded to yield a silica sand with generally sharper grains than the natural grains. Quartzite and sandstone can be shaped for various types of abrasive stones and wheels. Quartz, quartzite, and sandstone are abundant in California,

but have not been mined as abrasive materials in appreciable quantities. (See section on quartz and quartzite in this volume.)

**Pebbles for Grinding.** Between 1915 and 1948, more than 65,000 tons of pebbles for grinding mills was obtained from placer deposits in California. About four-fifths of this material was produced between 1915 and 1918 when imports from foreign sources were cut off during World War I. Although adequate supplies of suitable grinding pebbles still exist in California, they have not been produced for this purpose since 1948.

Hard, dense, tough, relatively fine-grained rocks, that are resistant to wear and wear evenly, make the best pebbles for grinding. Such pebbles generally consist of flint or quartzite but other types of rock such as rhyolite, granite, basalt, and various metamorphic rocks have proved satisfactory. Pebbles that range from 3 inches to 6 inches in diameter are marketed in specific sizes within that range.

Grinding pebbles are used mostly where size reduction must be obtained with a minimum of iron contamination. They have been used for grinding feldspar, talc, soapstone, cement clinker, chalk, quartz, sand, sandstone, and in gold mills. Iron and steel balls have replaced natural pebbles for many uses because the iron contamination has been found to be less detrimental than formerly believed. Porcelain balls are used in some mills.

The principal source of grinding pebbles in California has been along the shoreline between Oceanside and San Diego in San Diego County, where pebbles that were originally derived from granite and metamorphic rocks have been concentrated along the beaches by strong wave action. The pebbles are hand selected and sorted into specific sizes. The Crystal Silica Company now markets these pebbles as filter aids (see section on special sands in this volume). When last sold as grinding pebbles (about 1948) the price for pebbles between 3 and 6 inches in diameter was \$65 per ton, f.o.b. Oceanside. Pebbles also have been obtained from stream gravels in Calaveras, Fresno, Sacramento and Siskiyou Counties, mostly for use in nearby mills.

The principal sources of imported grinding pebbles are beach deposits of flint in Denmark, Belgium, and France. These are local concentrations of flint derived from chalk beds that are exposed in cliffs along the ocean (Metcalf, 1940). The pebbles are hand selected and sorted.

Domestic sources of pebbles for grinding are deposits in Minnesota, North Carolina, Texas, Washington, and Wisconsin. Quartzite, granite, and flint quarried from these sources are supplied as crude and rounded material. The principal domestic supplier of pebbles is Jasper Stone Company, Sioux City, Iowa, whose quarry is near Jasper, Rock County, Minnesota. Dense, fine-grained quartzite is mined and supplied both in crude form and artificially rounded form in several sizes. This material is marketed in California (1956) through wholesale dealers for the following approximate prices, f.o.b. Minnesota, in carload lots, plus freight, crating charges, and handling charges:

Egg-shaped, 2½" diameter	-----	\$49.00 per ton
Rounded, 2½" diameter	-----	\$69.00 per ton
Cubes, 3" x 4"	-----	\$39.00 per ton



*Miscellaneous Abrasives.* Diatomite, which is discussed more fully elsewhere in this volume, is used as a mild abrasive in hand soaps, and cleansing compounds, in silver and other metal polishes, in dental powder and pastes, and on safety-match heads and boxes. Of the 300,000 or more tons produced in the United States in 1954, less than one percent was used for abrasive purposes.

Although feldspar, kaolin, and talc are used for abrasive purposes, such markets are small. Ground feldspar, which is slightly softer than glass, is the main ingredient in some household cleansers. Kaolin has been used in silver polishing compounds. Some of the talc produced in California is used as an abrasive for polishing soft metals, leather, and rice grains. Each of these commodities is discussed in a separate section of this volume.

Dacite porphyry from near Corona, Riverside County, is quarried, crushed, and marketed mainly as roofing granules by Minnesota Mining and Manufacturing Company. As the crushed fragments are tough and angular they also have been found useful as an impact abrasive.

#### ARTIFICIAL ABRASIVES

Most artificial abrasive material is manufactured by combining two or more minerals or elements to form substances that are useful for their abrasive characteristics. Some artificial abrasives, however, are made by changing the shape of a substance to a more useful form, e.g. chilled shot from cast iron. Artificial or manufactured abrasives include three general types of products—electric furnace products, metallic abrasives, and chemical precipitates.

Large tonnages of artificial abrasives, principally electric furnace products, are consumed annually in California although none is manufactured in the state. The materials are brought into the state and consumed in the form of loose grains, bonded products (e.g. abrasive wheels), and coated abrasive products. Nearly every industry that manufactures products made of wood, plastic or metal uses electric furnace abrasives in one or more forms. Metallic abrasives and chemical precipitates are also consumed in California, but probably much less abundantly than electric furnace products.

Three products of fusion in electric furnaces are useful as abrasive agents. Of these, silicon carbide and fused alumina are the most common and boron carbide is much less so. Silicon carbide ( $\text{SiC}$ ) is extremely brittle and is exceeded in hardness (9.5 to 9.75) by only diamond and boron carbide. It is manufactured by fusing a mixture of crushed coke, silica sand, common salt, and sawdust, all of which are available from sources in California. Fused alumina is artificial corundum ( $\text{Al}_2\text{O}_3$ ). It is ordinarily referred to merely as alumina. It has a hardness of 9.2 to 9.6 and is considerably tougher than silicon carbide. A mixture of calcined bauxite, coke and iron borings is fused by means of electric arcs from carbon rods. Boron carbide ( $\text{B}_4\text{C}$  or  $\text{B}_5\text{C}$ ) is made by fusing dehydrated (anhydrous) boric acid ( $\text{B}_2\text{O}_3$ ) crystals with high-grade petroleum coke in the electric furnace. The raw materials necessary for the manufacture of boron carbide are available in California.

Electric furnace products have partly replaced nearly every abrasive material in some uses. Abrasive grains of silicon carbide and fused alumina are used for grinding,

lapping, drilling, rubbing, polishing, and as impact abrasives. They are used in coated abrasive products and in bonded wheels and stones. Boron carbide is used in grain and powder form and has replaced the use of diamond for certain applications.

The metallic abrasives are principally crushed steel, steel shot, and angular steel grit; and steel, copper, and brass wool. Crushed steel is made from brittle, high-carbon and crucible sheet steel. Steel shot is made of high quality cast iron, and angular steel grit is crushed steel shot. Steel, brass and copper wool are made into various finenesses by shaving or scraping continuously moving wire with fixed cutting tools.

Steel shot is used for sawing, grinding, and polishing stone, and smaller shot and angular steel grit are used as impact abrasives to clean metal castings, forgings, and metal parts. Steel wool is used for finishing wood and painted surfaces, and soft metal surfaces. Steel, brass, and copper wool are utilized as household cleansers and scouring agents.

Several chemical precipitates are used as abrasive agents in fine-grain sizes. Their main use is as polishing and buffing agents. Crocus and rouge, both iron oxides, are utilized in powders and pastes for polishing and finishing precious metals and stones. Some is used in coated abrasives. Other precipitates used as abrasives are chromium oxide, tin oxide, cerium oxide, manganese dioxide, magnesia, lime, and calcium carbonate. These agents have a wide variety of uses such as polishing and finishing glass, and buffing metals, plastics, and precious stones.

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# ALUMINUM

BY GEORGE B. CLEVELAND

Aluminum, the second most abundant metal in the earth's crust, is found in nearly all rocks. Only under special geologic conditions, however, does it occur in large high-grade deposits that can be economically worked as a source of the metal. At present the only important ore of aluminum is bauxite. The principal domestic deposits of bauxite are in Arkansas, Georgia, Alabama, and Mississippi. These contain only 2½ percent of the world's reserves, and many cannot compete either in quality or price with foreign imports. In 1955, the domestic deposits supplied only about 26 percent (1,818,038 long tons) of the bauxite consumed in the United States. The balance (5,221,008 long tons) was drawn principally from South America, notably from the Guianas, and from the Caribbean Islands of Jamaica and Haiti. The United States ranks first in the production of primary aluminum metal, supplying nearly 48 percent of the world total of 3,050,000 tons in 1954.

The known occurrences of bauxite in California are limited to small deposits which are associated with fire clay. None of these deposits have proved large enough to have been developed as a commercial source of aluminum; nor has this metal been recovered from any raw material mined in California. Other alumina-rich deposits, principally the large anorthosite bodies in the southern part of the state and the widespread alumina-rich clays, constitute potential reserves that may eventually yield aluminum on a commercial basis.

*Geology and Mineralogy of Bauxite.* Bauxite is a colloidal mixture composed of various proportions of the minerals gibbsite ( $\text{Al}(\text{OH})_3$ ) and the dimorphic forms boehmite and diaspore, both ( $\text{AlO}(\text{OH})$ ) (Palache et al., 1944, p. 667). Common impurities are rutile, siliceous minerals such as kaolinite and quartz as well as the iron oxides—limonite, hematite and goethite—and the carbonate minerals calcite, magnesite and siderite. Bauxite is gray, cream, yellow, dark red or earthy brown, is normally pisolitic or oölitic, and generally has a mottled appearance.

Bauxite is a residual product formed by the deep weathering of aluminous rocks under tropical conditions, and is commonly a constituent of lateritic soils. Under these extreme conditions of weathering, the silica and iron are partly removed, water is introduced and alumina ( $\text{Al}_2\text{O}_3$ ) titanium and iron oxides are concentrated (table 1, analyses 7-10). Climate, parent rock, chemical composition of the groundwater, surface of formation, drainage and time are all contributory factors in bauxite formation (Bateman, 1950, p 215-216). The principal parent rocks that have been altered to bauxite are nepheline syenite, granite, clay-bearing limestone, diorite, basalt, shale, clay, and dolerite.

Bauxite develops in areas that have a savanna-type tropical climate, and many of the world's bauxite reserves are in the tropics in such countries as Jamaica, Gold Coast, and Brazil. "Fossil deposits" such as those in Hungary, France, China, Yugoslavia and the United States, occur in areas where a tropical climate prevailed during the geologic past, but which today have another type of climate. Bauxite deposits range in age from Devonian to Recent, but most are late Mesozoic to early Tertiary. The domestic deposits are Eocene in age.

Bauxite deposits have been divided into three types: blanket, interstratified, and pocket. Blanket deposits are generally horizontal, near the surface and beneath a thin soil cover in areas in the late stages of erosion. The deposits in the southeastern United States and Gold Coast are examples of this type. Interstratified deposits are buried with other sediments and commonly occur as layers or lenses. In general, interstratified deposits are more highly indurated than those of the blanket type, owing to the weight of overburden. Bauxite occurrences in Arkansas, the Guianas and the minor deposits of California are of the interstratified type.

Pocket deposits are irregularly shaped bodies formed in local depressions some of which are solution cavities. Some are surficial and some are buried features. Pocket deposits commonly have formed on limestone, dolomite

Table 1. Analyses of high-alumina materials.

	(1)	(2)	(3)	(4*)	(5*)	(6*)	(7)	(8)	(9)	(10)
$\text{Al}_2\text{O}_3$ .....	27.32	26.96	27.3	42.48	46.52	36.13	53.9	53.87	64.6	53.06
$\text{SiO}_2$ .....	55.23	56.42	49.9	42.17	30.35	48.93	8.8	4.52	1.20	0.51
$\text{Fe}_2\text{O}_3$ .....	0.12	0.47	2.1	1.26	3.33	1.15	5.7	8.16	1.2	17.50
$\text{TiO}_2$ .....	0.04	0.08	0.3	--	--	--	2.3	--	--	2.10
$\text{CaO}$ .....	9.58	8.20	13.2	0.16	0.36	0.36	--	--	--	--
$\text{MgO}$ .....	tr.	tr.	0.6	tr.	0.10	0.21	--	--	--	--
$\text{K}_2\text{O}$ .....	0.39	0.97	0.6	0.16	0.16	--	--	--	--	--
$\text{Na}_2\text{O}$ .....	5.64	5.48	3.9	†0.96	0.03	†0.87	--	--	--	--
$\text{H}_2\text{O}$ .....	0.55	0.63	--	--	--	--	28.7	24.86	31.8	26.83

- (1-2) Anorthosite, Los Angeles Co., California.  
 (3) Anorthosite, Laramie, Wyoming.  
 (4) Bauxitic clay, Amador Co., California.  
 (5) Bauxitic clay, Riverside Co., California.  
 (6) Alumina-rich clay, Alameda Co., California.  
 (7) Bauxite, Saline Co., Arkansas.

- (8) Bauxite, Cherokee Co., Alabama.  
 (9) Bauxite, Surinam (Netherlands Guiana).  
 (10) Bauxite, Claremont, Jamaica.

\* Moisture-free basis.  
 † Total alkalies by difference.

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and clay and are also known on igneous rocks. Pocket deposits occur in France, Yugoslavia, Hungary and Italy.

*Occurrence of Bauxite Substitutes.* Aluminum has been produced experimentally or on a small-scale commercial basis from anorthosite, alunite, nepheline syenite, leucite, high-alumina clays, andalusite, and aluminous shales. When bauxite reserves become depleted, one or more of these materials will be extensively developed on an economic basis. Other raw materials that may become sources of aluminum are wavellite and diaspore. The urgent need for aluminum during World War II prompted investigation into such bauxite substitutes in this country and in Russia, Sweden and Japan. Small tonnages of alumina were produced from high-alumina clays at a pilot plant in Harleyville, South Carolina. Clay was also the raw material utilized in an aluminum recovery plant at Salem, Oregon. A plant was operated at Salt Lake City early in the war to recover alumina from alunite. Alunite from the Izu Peninsula also provided the ore for aluminum recovery in Japan, and Russia planned a similar operation to utilize alunite from Azerbaidzhan. During 1943, a pilot plant to produce alumina from anorthosite using the lime-soda-sinter process was constructed near Laramie, Wyoming. War-time shortages prompted Sweden to produce aluminum from andalusite. Russia recovers alumina from nepheline syenite tailings at apatite mines on the Kola Peninsula (U. S. Bur. Mines, 1953, p. VII—7).

The Anaconda Aluminum Company is experimenting (1956) with the recovery of aluminum from domestic alumina-rich clays. A large pilot plant in Montana will process raw materials mined in Idaho.

Although California contains no known deposits of clay that compare in alumina content with the high-alumina or diaspore clays, some of the fire clay described in the section on clay in this volume can be classified as alumina-rich clay. The high-alumina clays generally contain more than 40 percent alumina and diaspore clays contain 50 percent or more alumina. The alumina-rich fire clays from California deposits range from about 30 to 40 percent alumina.

As indicated in the discussion on clay, these deposits are in the Eocene Ione formation which occurs along the western foothills of the Sierra Nevada, the Paleocene Silverado formation exposed in the Alberhill-Corona area of Riverside County and in the Eocene Tesla formation in eastern Alameda County. These clay beds vary in their alumina content and the higher grade material would have to be selectively mined.

In 1942 the U. S. Bureau of Mines drilled a ten-acre area near the town of Ione, Amador County, to explore for high-alumina clay and revealed an estimated 53,800,000 tons of clay averaging 23.6 percent alumina and 2.4 percent iron on a dry basis (Turner, 1950, p. 287). Additional reserves in the Ione formation have been noted by Allen (1929, p. 379), Pask and Turner (1952, p. 22) and Dietrich (1928, pp. 51, 354-355). Sutherland (1935, p. 74, 85) reports that nine clay analyses from the Alberhill area of Riverside County range from 14.97 percent to 36.06 percent in alumina content and Dietrich (1928, p. 354-355) reports analyses from 25 clay samples which contain from 15.19 percent to 46.52 percent

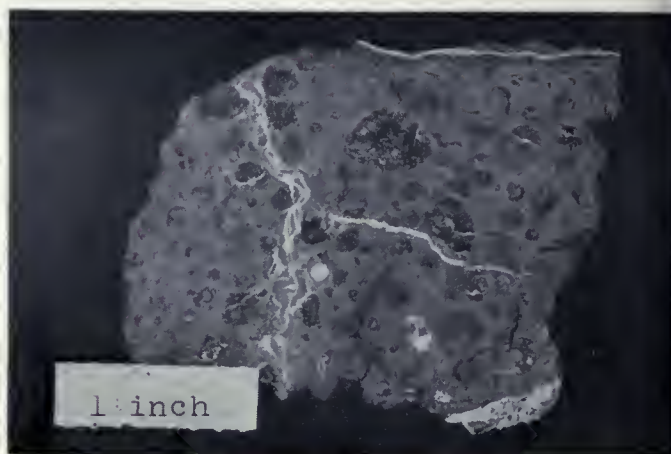


FIGURE 1. Alumina-rich laterite from Ione, Amador County, California, illustrating pisolites and general mottled appearance. This material ranges from about 30 to 40 percent alumina. Photo by Mary Hill.

alumina averaging 28.53 percent on a dry basis. Huey (1948, p. 60) and Allen (1941, p. 274-277) describe alumina-rich clays from the Tesla quadrangle, Alameda County; three representative samples reported by Allen average 35.93 percent alumina.

The alumina-rich clays of California are used principally by the ceramic industry. They occur, associated with other fire clays, in tabular bodies a few tens of feet thick and as much as several thousand feet in greatest diameter. These clays are principally sedimentary in occurrence, but residual deposits are known at Ione in Amador County and at Alberhill in Riverside County. In general the clays are intercalated with sand and sandy clay and in some localities with lignite coal. Where ceramic clay is mined, the overburden is relatively thin, being generally less than 20 feet thick lying over a clay bed that might be as much as 100 feet thick. The largest operations utilize heavy earth-moving equipment such as carryalls and power loaders to mine the clay.

The relatively high price of alumina-rich clays is supported by the demands of the ceramic industry and precludes their use as an ore of aluminum in the near future. Furthermore, the concentration of alumina in bauxite is nearly twice as much as the alumina content of the alumina-rich clays.

Recent studies by the California Division of Mines concerned with the concentration of aluminum and other metals in lateritic soils have greatly increased the known areas of lateritic weathering in the state. A large part of northern California, especially in western Klamath Mountains area and along the western foothills of the Sierra Nevada were subjected to lateritic weathering between late Cretaceous and early Tertiary time. Because of the close association of laterite and bauxite elsewhere in the world this part of the state may contain bauxite deposits (see section on nickel in this volume).

The only large anorthosite bodies known in California are exposed in the western San Gabriel Mountains of southern California and have a combined outcrop area of about 50 square miles (Oakshott, 1954). Anorthosite is a rock composed principally of plagioclase feldspar,





FIGURE 2. Typical anorthosite terrane in Soledad Canyon, Los Angeles County, California.  
Photo courtesy Southern Pacific Railroad.

generally labradorite or calcic andesine. It may contain small amounts of pyroxenes, ilmenite and magnetite. The San Gabriel Mountain anorthosite is composed of calcic andesine (97 percent) with small amounts of apatite and zircon (Higgs, 1954, p. 178). Table 1 shows typical analyses from these bodies as well as an analysis of Wyoming anorthosite that was used as an experimental source of aluminum during World War II.

In California, nepheline syenite has been reported from the northern Death Valley area of Inyo County by McAllister (1952, p. 31; 1955, p. 14). A typical analysis shows 21.72 percent alumina, 59.14 percent silica and 1.69 percent iron. The rock has a combined outcrop area of about two square miles.

Andalusite has been reported from 11 counties in California but the only important deposit is in the White Mountains of eastern Mono County (Murdoch and Webb, 1948, p. 47). This mine has produced rock containing greater than 60 percent andalusite, but this was very expensive to mine and the known andalusite reserves are of considerably lower-grade. The mine, therefore, cannot be considered a potential source of aluminum.

**Recovery Processes.** Before metallic aluminum can be recovered from alumina ( $\text{Al}_2\text{O}_3$ ) the crude ore must be beneficiated first to remove clay, iron oxides and titanium and second, to extract the alumina. Two principal methods are used to free the alumina: (1) the alkaline method used for bauxitic ore rich in alumina and free from excessive amounts of silica and iron and (2) the acid methods suitable for non-bauxitic, low-alumina, high-silica ores.

Only the Bayer process, or alkaline method, is now used to extract alumina from bauxitic ores. In this process the ore is ground and treated with sodium hydroxide which extracts the aluminum in solution as a sodium aluminate. The insoluble residue of iron and silica is filtered off and, from the clear solution, aluminum is precipitated as the hydrated oxide. The precipitate is

washed to remove soda and calcined to anhydrous alumina.

About sixty acid leaching processes have been developed to win aluminum from non-bauxitic ores. Three primary objectives are common to these processes: (1) to render the ore acid-soluble (2) to free the alumina from the enclosing gangue and impurities, and (3) to recover the reagents for reeyeling. Acid leaching methods utilize sulfuric, sulfurous, nitric, or hydrochloric acids, and much of the acid is lost by reaction with iron, alkali-earths and phosphorous impurities. Moreover, the formation of new compounds necessitates costly refining procedures. Ores that can be treated by acid processes are: alumina-rich clays (25 to 35 percent  $\text{Al}_2\text{O}_3$ ), leucite, high-silica bauxite, aluminous shales, alunite (more than 25 percent  $\text{Al}_2\text{O}_3$ ), and anorthosite (25 to 30 percent  $\text{Al}_2\text{O}_3$ ).

Among the more promising methods to recover aluminum from non-bauxitic ores is the lime-soda-sinter process developed at a pilot plant in Wyoming to utilize anorthosite (Brown, et al., 1947). Finely ground anorthosite, limestone and soda ash are sintered to form water-soluble sodium aluminate and water-insoluble calcium silicate. The sodium aluminate is leached with alkaline solutions and aluminum trihydrate is precipitated by passing carbon and air through the pregnant solution. The trihydrate is calcined, forming anhydrous aluminum oxide. Other compounds such as soda ash and potassium sulfate are recovered in the end process.

The Hall-Heroult electrolytic process is employed to produce metallic aluminum from alumina. In this process, the alumina is dissolved in molten cryolite ( $\text{Na}_3\text{AlF}_6$ ) in an electrolytic cell and reduced to the metallic state by passing a current between electrodes.

The principal deterrent to the use of most bauxite substitutes lies in their high ratio of silica to alumina and the initial concentration of alumina compared with the alumina content of bauxite. A high concentration of silica is incompatible with the alkaline (Bayer) leaching



process now in general use, as it promotes the formation of unusable sodium-aluminum silicates. The suitable, but more expensive, acid leaching processes do not dissolve any appreciable amount of the silica and therefore no undesirable alumina-silica products are formed. However, acid leaching has the disadvantage of taking into solution iron, phosphorus, and alkali-earth metals which interfere with the final electrolytic reduction.

The use of certain substitute materials is further restricted by their relatively high cost. This is especially true of alumina-rich clays. For the present, the large and easily tapped foreign supplies of bauxite dispel any large-scale replacement of substitutes. Increased consumption of aluminum and the steady elimination of technical and economic problems, however, point to the future utilization of other alumina-rich minerals.

*Uses.* The most useful properties of aluminum are low specific gravity, high resistance to corrosion, high electrical and thermal conductivity, ductility, high strength in alloys, and high reflectivity. Engle's (1945, p. 425) industrial marketing appraisal of aluminum lists more than a thousand common uses of this metal. Of the 3 billion or more pounds of aluminum produced in 1955 in the United States, building materials accounted for 19 percent; transportation, 17 percent; consumer durable goods, 13 percent; electrical uses, 8 percent; machinery and equipment, 7 percent; and packaging and containers, 5 percent (Chemical Week, 1955, p. 58).

Aluminum products can be placed in three main groups: (1) wrought products, (2) cast products, and (3) alloys and chemicals. The building industry is the principal civilian consumer of aluminum. Aluminum and its alloys are being used for the exterior facing on industrial buildings; as paneling and siding in home construction; in paint; and for doors, hardware, blinds, roofing, windows, insulation and awnings. The home appliances and materials that contain aluminum include refrigerators, vacuum cleaners, air conditioners, cooking utensils, outdoor furniture, and fabrics used for draperies and upholstery.

In the automobile industry, aluminum is now used for such parts as pistons, door handles, body trim and bearings which were formerly constructed of steel, chromium and copper. Certain makes of autos contain nearly 100 pounds of this metal in each unit and the average passenger car contains about 30 pounds. Builders of trucks, trailers, buses, railroad cars and ships are using aluminum sheeting as an attractive exterior covering on their products.

Aluminum may be substituted for tin and steel in containers. Steel cans for processed food have been developed with aluminum rather than tin coatings. Motor oil is sold in cans made entirely of aluminum. Although all-aluminum cans are more expensive than steel, the saving in shipping weight and the salvage value of the metal may offset the difference in cost. Aluminum containers formed from pressed foil are receiving wide application in the frozen food industry.

A recently developed dry cell battery contains an aluminum can rather than the conventional zinc can, thus making use of aluminum's low electrochemical equivalent and high electropotential. Aluminum wire has partly replaced copper in electric power transmis-

sion. Although aluminum has lower electrical conductivity than copper, smaller gauge aluminum wire gives equal performance with savings in weight and initial cost.

Chemicals such as sodium aluminate, zeolite, aluminum sulfate, aluminum nitrate, and aluminum chloride constitute a large part of the 85,000 tons of aluminum used yearly in industrial chemicals. Nearly a third of this total is used to make synthetic cryolite and aluminum fluoride—chemicals essential to the production of aluminum metal.

Military applications account for about one-third of the total amount of aluminum consumed in the United States. Most of this goes into aircraft construction, but other uses include bridges, ships, rockets, airborne equipment, fuel pipe and smaller items such as cooking equipment used by the ground troops.

Bauxite, at high temperatures, fuses to corundum and is widely used in the manufacture of abrasives. The use of the synthetic material far exceeds that of natural corundum. Bauxite is also used in high-alumina refractories, as a substitute for Missouri diaspore. About 700,000 tons a year of aluminum sulfate are produced directly from bauxite and there is a growing market for its use in absorptive compounds for the petroleum industry, in high-alumina cements and as a flux in the steel industry.

Although about 90 percent of the alumina produced in the United States is reduced to metallic aluminum, a large part of the balance is used to make silica-alumina cracking catalysts, white artificial abrasives, industrial chemicals and refractories for the ceramic industry.

Prior to 1940, nearly all the aluminum used in the United States was produced by the Aluminum Company of America. Early in World War II, the Reynolds Aluminum Company, then a fabricator of metal products, entered the field as a fully integrated company and in 1946 it was followed by the Kaiser Aluminum and Chemical Company. In 1955, Anaconda Aluminum began production of primary metal at Columbia Falls, Montana.

*Markets.* The production of primary aluminum is dependent upon abundant electrical power and bauxite ore. The aluminum industry, in order to balance these two economic factors, has located plants in three principal areas—Washington, Oregon, and Montana; Texas, Arkansas and Louisiana; and in New York, North Carolina, Alabama and Tennessee. The cheap electrical power of the Pacific Northwest offsets the cost of transporting raw materials from the Caribbean and the Gulf Coast. Eastern plants, although deriving part of their electricity from coal which is relatively expensive, are in the heart of a large aluminum consuming area. The Gulf Coast plants derive their power from electric plants that consume natural gas or lignite and benefit from their close proximity to Jamaican and Arkansas ores.

Aluminum raw material and formed stock is shipped throughout the United States for final fabrication. For example, one aluminum company converts Jamaican bauxite to alumina at Baton Rouge, Louisiana; the alumina is reduced to pig at New Orleans or at Mead or Tacoma, Washington. The pig is converted to rod, bar, wire or ingot in Ohio. Ingot stock is shipped to Pennsyl-



nia for forgings. Extrusions are made in Maryland sheet and plate at Trentwood, Washington. Sheet aluminum from Trentwood is shipped to West Virginia and to Permanente, California to be milled into foil. The basic forms are sold to numerous manufacturers for making useful products.

Aluminum is produced in a few large integrated plants and they are the principal markets for bauxite. Generally, these plants draw their raw materials from company owned or controlled deposits. Commercial amounts of bauxite have not been produced in California because the known deposits are too small for large scale commercial development and abundant and cheap electrical power is lacking. Under present marketing conditions it would be difficult to develop a bauxite deposit in California. The railroad freight charges to transport the ore to alumina extraction and aluminum reduction plants in other states would make it economically unfeasible. Small amounts of bauxite have been used in California in making zeolite water softeners and local markets could possibly be developed that would utilize bauxite for abrasives, chemicals or absorptive compounds. However, it seems unlikely that any large scale development could be supported by the present demand. Before aluminum can be produced in California from the nonbauxitic raw materials previously described, the cost of producing it in this state will have to approach the price of aluminum. Although progress has been made on the recovery of aluminum from nonbauxitic ores, the high cost of plant facilities, transportation equipment and raw materials would inhibit a rapid changeover to a new process. The large initial capital investment necessary to enter the aluminum industry would be another major deterrent to all but the largest companies.

**Prices.** In 1940 the price for 99 percent plus primary aluminum ingots, was 18.7 cents per pound. From 1942 until 1947, the price was stabilized at a low of 15.0 cents per pound, but by 1952 the price had reached 20 cents and by middle 1955 to 24.4 cents. In September of 1956 the price was 27.1 cents per pound. In October 1956, domestic bauxite sold for about \$8 per long ton at the mine and imported bauxite was about \$6 per long ton. o.b. British Guiana. Abrasive grade bauxite ranged from \$17 per long ton for domestic ore to \$19 for imported ore. Refractory grade imported ore brought about \$24 per long ton. Although the base price of aluminum has increased, it has not undergone the radical fluctuations of other competitive materials and its price history is compatible with the country's general economic trend.

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## ANTIMONY \*

By HAROLD B. GOLDMAN

Though antimony occurs at numerous localities in California, and was mined as early as 1887, only a few hundred tons of the metal have been obtained from mines within the state. More than half of the total output was mined during the period 1915-17 under high wartime prices. Since World War I, antimony production has been negligible, notwithstanding the urgent demand and high prices of World War II. Antimony concentrates from out-of-state sources, however, were melted in California. Deposits in Kern and Inyo counties have been the principal antimony sources in the state.

### MINERALOGY AND GEOLOGY OF DEPOSITS

Stibnite ( $\text{Sb}_2\text{S}_3$ ) is the only antimony mineral of commercial importance, although its oxidation products, pyroantimonite ( $\text{Sb}_2\text{O}_4$ ), senarmontite ( $\text{Sb}_2\text{O}_3$ ), and valentinite ( $\text{Sb}_2\text{O}_3$ ) contribute to the value of some ores. Tetrahedrite [ $(\text{Cu}, \text{Fe})_{12}\text{Sb}_4\text{S}_{13}$ ], cinnabar ( $\text{HgS}$ ), and pyrargyrite ( $3\text{Ag}_2\text{S} \cdot \text{Sb}_2\text{S}_3$ ) are among the many antimony minerals of minor importance as sources of antimony.

Most concentrations of antimony occur as stibnite-bearing quartz veins. Such veins have formed in a wide variety of rock types but generally exist in regions in which igneous rocks are abundant. The stibnite is characteristically pockety and irregularly distributed in rather small concentrations. Most quartz-stibnite veins have formed at shallow depths and at relatively low temperatures. They appear to have been formed by hot seeping solutions genetically related to the nearby igneous bodies. Other minerals commonly present in the shallow veins, though in small amounts, are pyrite ( $\text{FeS}_2$ ), sphalerite ( $\text{ZnS}$ ), arsenopyrite ( $\text{FeAsS}$ ), tetrahedrite [ $(\text{Cu}, \text{Fe})_{12}\text{Sb}_4\text{S}_{13}$ ], and cinnabar ( $\text{HgS}$ ). Minor amounts of silver and gold also occur in some of these veins. A more deep-seated origin has been ascribed to some antimony deposits that occur within or near plutonic igneous rocks. The igneous rocks with which most of the world's antimony deposits are associated range in age from late Cretaceous to Tertiary. Antimony deposits probably were comparably abundant in formations of even greater age, but are presumed to have been eroded away.

Replacement deposits of antimony in shale and limestone are also common. In some replacement deposits, stibnite is subordinate to galena and other lead-bearing minerals. Stibnite, with cinnabar, may be found in hot springs deposits.

The largest deposit of antimony ore in the United States is in the Yellow Pine district, at the Yellow Pine mine, Valley County, Idaho. More than 80 percent of the domestic production from 1932 to 1952 was obtained from this mine where stibnite, associated with gold and silver, occurs in veins throughout wide shear zones in quartz monzonite of the Idaho batholith. These veins average about one percent antimony. When the price of antimony was low the ore was mined chiefly for gold.

When the price of antimony was more than 20 cents per pound, the antimony was valued more than the gold. In 1940, White (1940a, p. 248) estimated that the minable reserves were 2,818,000 tons of ore containing 25,970 tons of recoverable antimony. The U. S. Bureau of Mines and Geological Survey (1951, Chapt. III, p. 7) estimate the total domestic reserves at 80,000 to 100,000 tons of antimony, half of which are in the Yellow Pine district. Other deposits in the United States occur in the Humboldt Range, Nevada; Baker County, Oregon; and in Garfield County, Utah.

The bulk of the world's production of antimony has been obtained from China and Bolivia. China was the principal source until 1937, supplying nearly two-thirds of the world's output. The world's chief reserve of antimony is in the Hsi-K'uang-shan field in Hunan Province. Here stibnite and quartz occur in fractures in a 500-foot bed of quartzite. The field is  $3\frac{1}{2}$  miles long by 2 miles wide and has been worked to a depth of 300 feet. The average antimony content is about 6 percent (U. S. Bureau of Mines and Geological Survey, 1951, an. 2, p. 12). China's reserves are estimated at 4 million tons of contained antimony, over 70 percent of the total world reserve (U. S. Bureau of Mines and Geological Survey, 1951, chapt. 3, p. 50). Since 1940, Bolivia has been the world's leading producer of antimony. The antimony occurs in numerous scattered deposits in a northwest-striking belt extending from Achacache north of La Paz southeast into Argentina. Quartz veins containing stibnite and antimony oxides occur in narrow long belts of fractured slates as much as 85 miles long and 1300 feet wide. The veins are 2 to 3 feet wide, and irregular. The highest-grade material occurs at vein intersections. The ore as mined contains about 10 percent antimony. Reserves are estimated at 500,000 tons of the metal (U. S. Bureau of Mines and Geological Survey, 1951, chapt. 3, p. 40).

The principal antimony deposits of Mexico are in the states of San Luis Potosí, Oaxaca, Querétaro, Zacatecas and Sonora. The deposits occur as replacements in limestone, and as fissure veins genetically related to volcanic rocks of intermediate to acidic composition. The highest-grade ore bodies consist of irregular masses, veinlets, and disseminations in limestone, and contain about 5 percent antimony. Reserves in Mexico are estimated at 500,000 tons of antimony. However, most of the ore is low grade containing antimony oxides that are uneconomical to process (U. S. Bureau of Mines and Geological Survey, 1951, chapt. 3, p. 26).

### LOCALITIES IN CALIFORNIA

Small, widely scattered deposits of antimony occur in several localities in California, principally in Kern, Inyo and San Benito Counties. Past production came mainly from the Wildrose Canyon deposits, Inyo County; the San Emigdio Canyon area, Kern County; and small deposits in the eastern part of Kern County. The largest reserves are in Wildrose Canyon, Inyo County; Antimony Peak, Kern County, and the Stayton district in San Benito and Merced Counties.

\* Partly extracted from a section by L. A. Norman, Jr. in California Div. Mines Bull. 156.



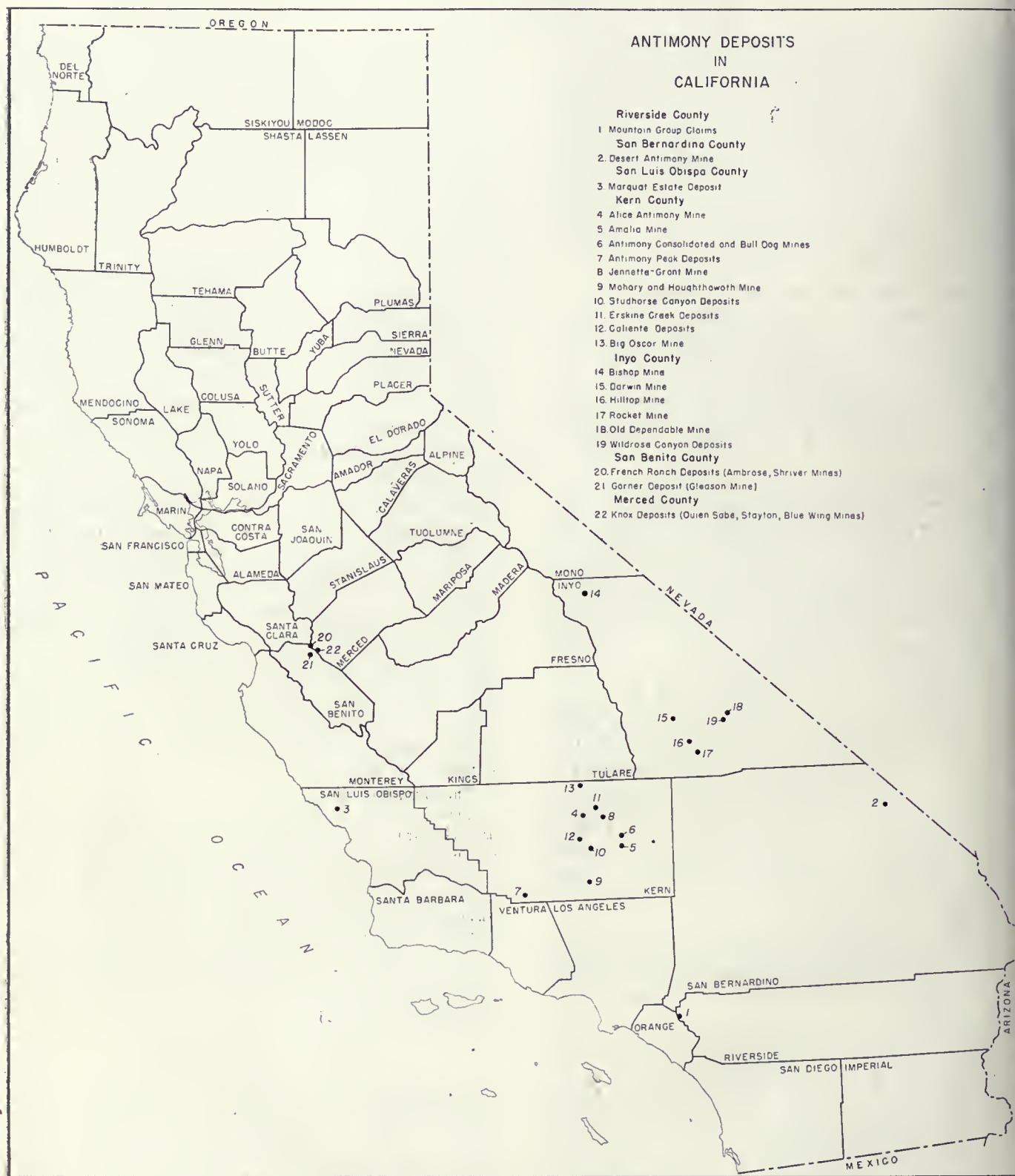


FIGURE 1. Map showing antimony deposits in California.



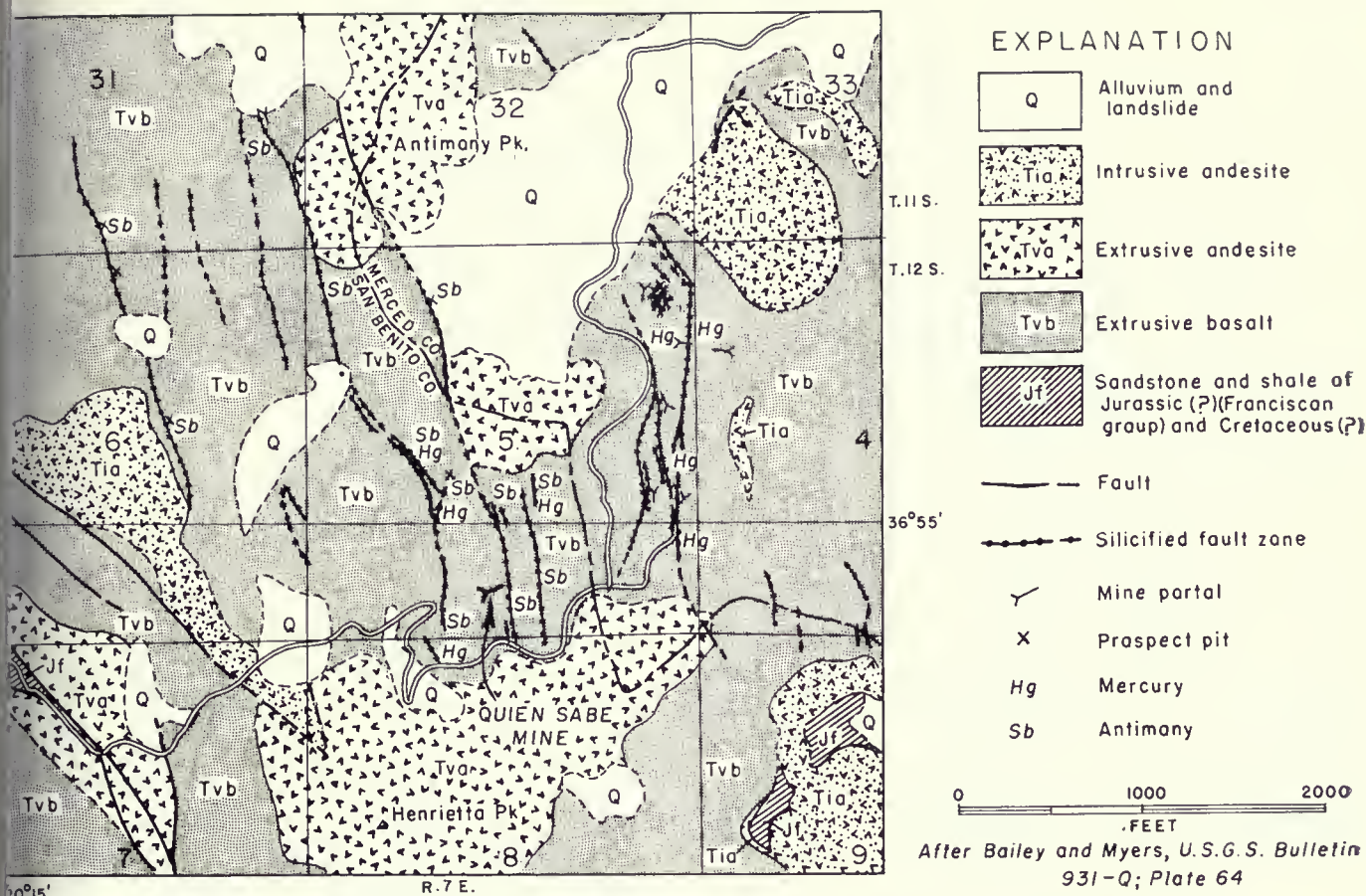


FIGURE 2. Geologic map of Stayton district, San Benito County. After U.S. Geol. Survey Bull. 931.

**Inyo County.** In Wildrose Canyon, which is in the Panamint Range, stibnite and its alteration products occur in zones of shearing and fracturing along the limbs and crests of anticlines in pre-Cambrian chlorite schist and amphibolite. The deposits are distributed throughout an area approximately  $\frac{1}{2}$  mile wide and  $\frac{3}{4}$  mile long. The ores are of two types: brecciated amphibolite containing from 1 to 2 percent antimony, and quartz veins containing from 5 to 10 percent antimony (White, 1940b, p. 320). The richest deposits are on the south side of the canyon in a vein system that extends for 200 feet. The veins range from less than an inch to 5 feet in width, averaging  $1\frac{1}{2}$  feet wide. The main vein has been worked to depths up to 50 feet in the Wildrose antimony mine. Stibnite-bearing quartz veins also occur on the north side of the canyon, 2 miles north of the Wildrose antimony mine. The main vein there is traceable on the surface for 200 feet and strikes N.  $10^{\circ}$  W. and dips  $70^{\circ}$  E. In three short adits drilled into the hillside, the vein averaged 2 feet in thickness. The reserves in the Wildrose Canyon area probably contain at least 1000 tons of antimony (U. S. Bureau of Mines and Geological Survey, 1951, chap. 3, p. 9).

Other deposits in Inyo County occur at the Old Dependable mine in Trail Canyon, Panamint Range; on the west slope of the Argus Range at the Hilltop, Rocket and Darwin mines; on the east slope of the Sierra Nevada near Bishop. At the Bishop mine pods of stibnite

about 8 feet in maximum dimension occur in a zone of fault gouge between rhyolite and limestone.

**Kern County.** In the San Emigdio Canyon area at Antimony Peak, Kern County, antimony deposits lie along a shear zone in quartz diorite exposed near the top of the peak. The zone is 2500 feet long and from 10 to 130 feet wide, averaging about 35 feet in width. It trends N.  $40^{\circ}$  W. and dips  $55^{\circ}$  to the south. The ore is irregularly distributed and occurs as small lenses and pods with their long axes parallel to the strike of the zone. Lenses several feet in width, when followed downward, commonly thin to a few inches or pinch out altogether. The higher grade ores contain stibnite, quartz, antimony oxides, and inclusions of country rock. Trenching and sampling by the U. S. Bureau of Mines in 1940 and 1941 revealed 19 lenses with an average length of 80 feet, a width of 8.5 feet and an average antimony content of 2.5 percent (Jermain and Ricker, 1949, p. 4). Reserves are estimated at 3000 to 9000 tons of antimony (U. S. Bureau of Mines and Geological Survey, 1951, chap. 3, p. 9).

Small deposits of antimony occur near the Kern River in the Havilah and Kernville districts and in the Mojave-Rosamond area, but the best of the easily recovered ore appears to have been removed and the reserves are probably small. Some native antimony was found in these districts (Murdoch and Webb, 1948, p. 50). Small ore bodies have been worked intermittently at the Alice mine in the Havilah district, the Amalia



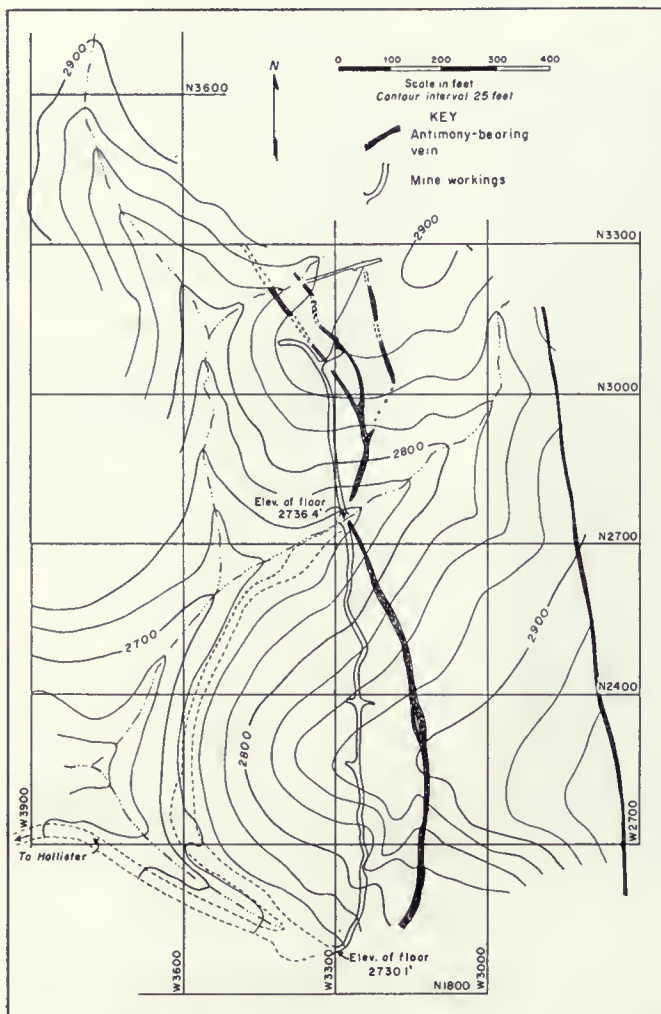


FIGURE 3. Map showing veins at Quien Sabe mine, San Benito County. After U.S. Bur. Mines Rept. Inv. 5192.

mine near Cineo, the Jennette-Grant mine in the Green Mountain district, Wiggins and Studhorse Canyon mines in Studhorse Canyon, the Rayo, Standard, Grace Darling, Tom Moore mines on Erskine Creek, the Mahary and Houghthawth near Rosamond, and at the Bull Dog and Antimony Consolidated mines north of Mojave.

**San Benito County.** The Stayton mercury-antimony district is in the eastern part of San Benito County but also includes parts of Santa Clara and Merced Counties. The district is approximately 4 miles wide by 6 miles long and lies in the north-central part of a dissected Tertiary volcanic field that extends over a hundred square mile area. The rocks of the area include Miocene (?) basaltic extrusive rocks that were arched into a northward-trending antiform, planed by erosion and capped by andesitic extrusive rocks. Quartz veins containing stibnite and cinnabar occur mainly in the basalts along north-trending faults in the central part of the district. The veins average 2 feet in width and range from a few hundred to several thousand feet in length and are bordered by a kaolinized and silicified breccia. This breccia is, in part, replaced and cemented by veins of

black chalcedonic quartz containing pyrite and small needles of stibnite. Small pods of stibnite have replaced the black quartz and filled fractures in it. The average antimony content is 1 to 3 percent (Bailey and Myer 1949, p. 48). The deposits are all on private ranches and none are held as mining claims. The property owners are the French Ranch (Ambrose and Shriver mines), Wiley Garner (Gleason mine), and R. B. Knox (Stayton, Blue Wing, and Quien Sabe mines).

In late 1949 and throughout 1950 the Cordero Mining Company of Palo Alto and the U. S. Bureau of Mines prospected the Quien Sabe mine on the Knox property with tunnels and drill holes. Ten cored holes ranging in depth from 150 to 359 feet and totaling 2483 feet were drilled and sampled by the Bureau of Mines (Wiebelt, F., 1956, p. 1). The antimony occurs as stibnite localized in northward-trending silicified fault zones in basalt and tuff. The veins, which dip westward from 44° to 60°, have been developed by more than 160 feet of drifts and crosscuts. Nine of the holes encountered antimony-bearing vein material. Seven of the holes penetrated a mineralized zone approximately 11 feet thick that assayed 1.7 percent antimony. This zone extended for a distance of about 200 feet down the dip of the vein below a tunnel which was driven 1200 feet along the strike (Wiebelt, 1956, p. 9). Overall exploration revealed an estimated 200,000 tons of ore averaging 3 percent antimony and a probable estimated reserve of 1 million tons of 3 percent antimony ore (Williston, S. H., 1956, personal communication).

**San Bernardino County.** The Desert Antimony mine near Mountain Pass is the only property that has been operated for antimony in San Bernardino County. Stibnite occurs in quartz veins in Archean granite gneiss. The veins 2 to 5 feet wide contain irregular aggregate and stringers of stibnite up to 2 feet wide. The ore is reported to have contained 15 to 20 percent antimony, sorted to a grade of 40 percent (Wright, L. A. and others, 1953, p. 59). Small tonnages were produced in 1927-28 and 1939.

Other minor ore bodies in the state have been worked at the Mountain Group claims in Riverside County, and the Marquat Estate deposit in San Luis Obispo County. Occurrences of antimony-bearing minerals in California have been tabulated by Murdoch and Webb (1948, p. 50).

#### HISTORY OF PRODUCTION

The deposit discovered prior to 1859 in San Emigdio Canyon, Kern County, was the first antimony discovered in the United States that proved to be of commercial value (Schrader, 1933, p. 662). From 1887 to 1954 this and other deposits in California have yielded a total production of antimony valued at slightly in excess of \$225,000 (Averill, C. V. and others, 1948).

The San Emigdio antimony mine in Kern County was first worked by the padres of the mission period. It was reopened in 1876 and a concentrating plant and smelter were erected to treat the ores which carried silver as well as antimony. This mine and other mines in the same area and in other districts in Kern County have been worked intermittently. Most of their productive periods have been during times of high metal prices, particularly in 1915-16, 1925, 1928, 1939-44. The



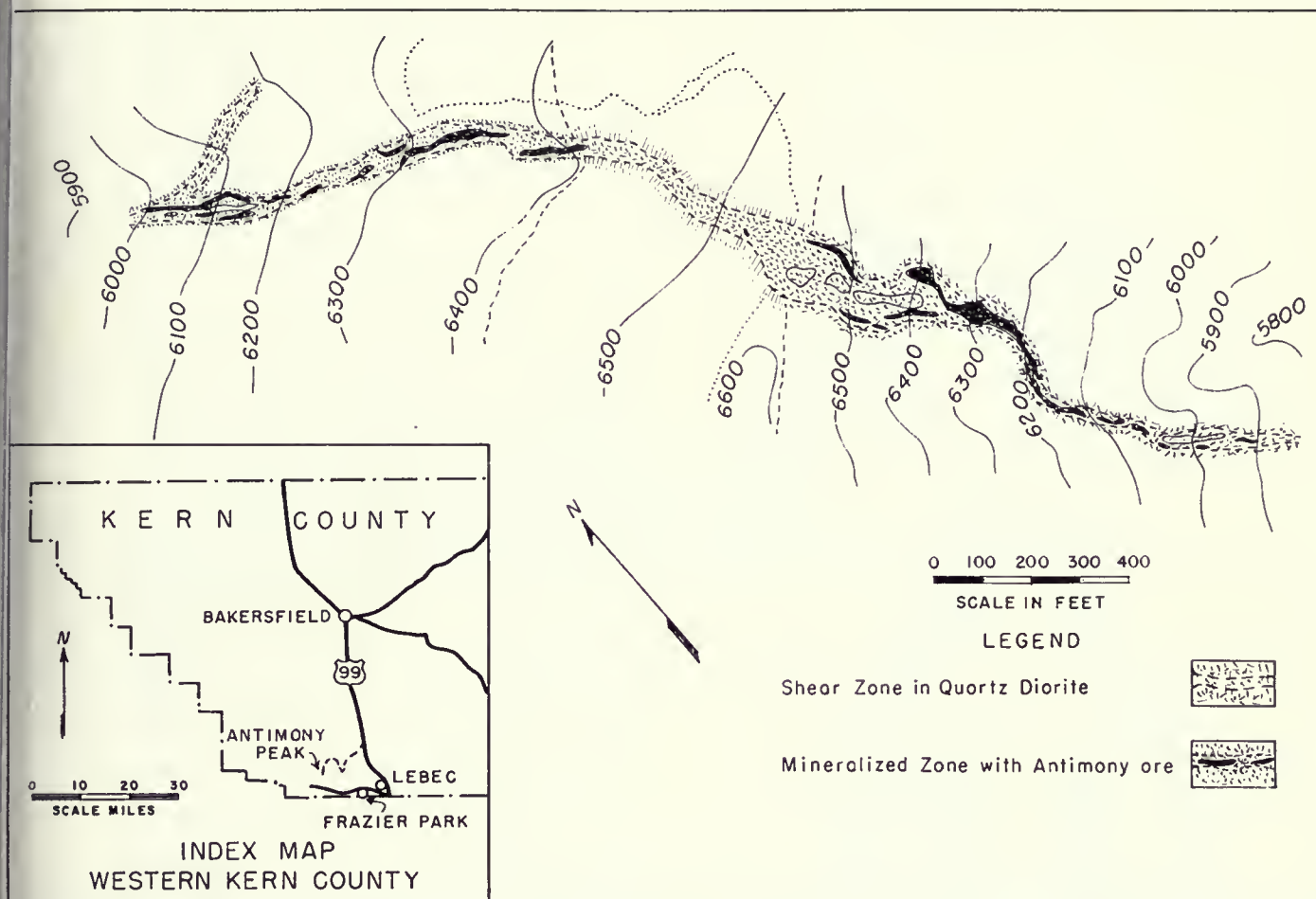


FIGURE 4. Map showing mineralized zone at Antimony Peak, Kern County. After U.S. Bur. Mines Rept. Inv. 4505.

total value of antimony production from Kern County is estimated at approximately \$80,000 (Tucker, Sampson, and Oakeshott, 1949, p. 206). The most recent activity in the county was in 1952 and 1953 when a few tons of antimony ore was mined but not shipped from the Bingo and Antimony Queen mines in the Caliente area and the Big Oscar mine in the Greenhorn Mountains.

During the 1915-17 antimony "boom" the Wildrose mine in Inyo County was the principal source of antimony in the state, yielding an estimated 4000 tons of ore (Tucker and Sampson, 1938, p. 378). Some of the ore was treated at a plant in Wildrose Canyon, but most of it was treated at a smelter in San Pedro. This mine has been little worked since 1918. During World War II there was a revival of production in the county principally from the Bishop, Darwin and Old Dependable mines. Since 1944 the only production in Inyo County was 5 tons of ore worth \$1467 from the Rocket mine in 1948.

The antimony deposits of the Stayton district, San Benito County, were first worked from 1870 to 1875. Cinnabar associated with the antimony was soon discovered in the area and work was concentrated upon the more valuable quicksilver ores. However, the antimony deposits were reopened in the periods 1894-95, 1916-17,

1927-28, and 1941-42. The amount of antimony produced is unrecorded, but the total is presumably only a few hundred tons. Since 1942 only quicksilver has been produced from this district.

The search for additional antimony deposits is being carried on through exploration assistance of the Defense Mineral Exploration Administration under the Defense Production Act. In 1953, a DMEA loan was granted to the Abaca Mining Company to explore the Big Oscar antimony prospect in Kern County. Only traces of antimony-bearing material were encountered by the exploration work. A portion of the Stayton district was test drilled by the U. S. Bureau of Mines in 1950; a DMEA loan was recommended but no ore was mined.

#### UTILIZATION

Antimony is a brittle, silvery-white metal with a melting point of 630° C., a low coefficient of expansion  $10.2 \times 10^{-6}$  at 0° C., and a Mohs' scale hardness of 3. Owing to its brittleness the metal is very seldom used alone in industry but advantage is taken of this property in alloys. Elemental antimony exists in two forms. Alpha antimony is a metastable form containing antimony trichloride in solid solution. This solid solution is known as "explosive antimony" because if heated or scratched, it transforms suddenly to beta form giving off clouds



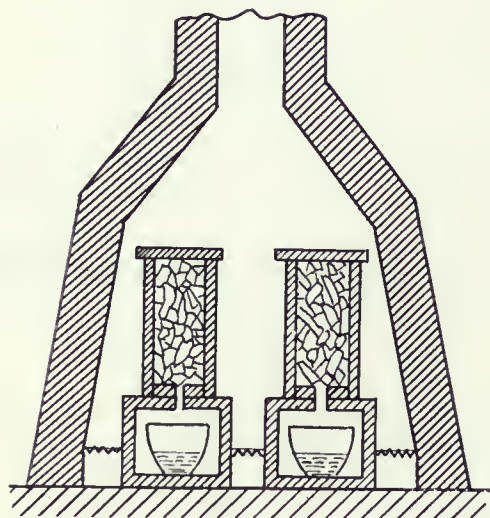
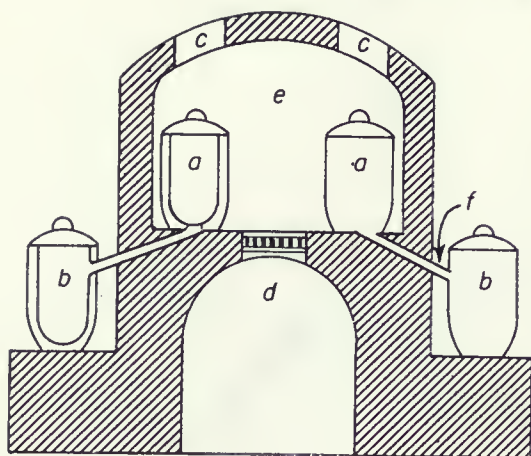


FIGURE 5. Furnace for liquating rich antimony ores.  
After Wang, *Metallurgy of Antimony*.

of antimony trioxide. This property has led to the use of antimony in flameproofed textiles and fireworks.

Antimony metal imports hardness and strength to softer metals when incorporated into alloys. The principal use for the metal is in antimonial lead employed in the manufacture of grid plates for lead storage batteries. Antimony is added to the lead plate because: (1) it gives a clear casting with more accurate and reproducible results than can be obtained with soft lead; (2) it resists sulfuric acid better; and (3) it is harder than soft lead and less subject to mechanical damage (Haskell, 1952, p. 21). Antimony also is widely used in bearing metals because lead-tin-antimony alloys possess the requisite hardness and have low melting points that enable them to be cast easily. Antimony is also used in type metal since the antimony hardens the type making it resistant to impact and wear, and counteracts the tendency of lead to contract during solidification of the alloy. Lead alloys, of which antimony comprises from 1 to 20 percent, are also used in cable sheathing, solder, ammunition, sheet pipe and other minor products. In 1954, approximately 40 percent of the primary antimony consumed by industry was in such metal products.

The principal industrial compounds of antimony are the trioxide  $\text{Sb}_2\text{O}_3$ , sulfide  $\text{Sb}_2\text{S}_3$ , and chloride  $\text{SbCl}_3$ . Peacetime uses of these compounds are mainly as opacifying agents in enamels, pigments in paints and lacquers and flame retardant in plastics and paints. During World War II and in recent years the largest single use of nonmetallic antimony was in preparing an antimony compound to render war and industrial fabrics and camouflage paints fire resistant. The compounds antimony trioxide or antimony chloride dissolved in an organic solvent quickly extinguish flames by a chemical reaction that releases smothering clouds of antimony trioxide.

Antimony trioxide is used as an opacifying agent for white enamels to give a brilliant finish and lessen the blistering effects of tin oxide which it replaces. The use of the oxides is due to their high refractive indices 2.04 and 2.09.

"Antimony white" the trioxide of antimony, which is formed as a very fine powder in the flues of antimony roasting furnaces, can be used as a pigment. A specially ground and prepared oxide of superior texture, opacity and whiteness is also produced for this purpose. Other pigment colors are obtained from the oxides and trioxides.

Antimony is also used in various forms in the manufacture of medicine, fireworks, ammunition primers, matches and rubber products. In 1954, approximately 60 percent of the primary antimony consumed by industry was in nonmetallic products. Table 1 shows the industrial consumption of primary antimony in the United States in 1954.

Table 1. Industrial consumption of primary antimony in 1954.\*

Product	Short tons antimony content	Percent of grand total
<b>Metal products:</b>		
Ammunition.....	5	.1
Antimonial lead.....	1,531	12.6
Battery metal.....	1,583	13.0
Bearing metal and bearings.....	816	6.7
Cable covering.....	156	1.3
Castings.....	70	.6
Collapsible tubes and foil.....	47	.4
Sheet and pipe.....	238	1.9
Solder.....	148	1.2
Type metal.....	613	5.0
Other.....	118	1.0
<b>Total metal products.....</b>	<b>5,325</b>	<b>43.7</b>
<b>Nonmetal products:</b>		
Ammunition primers.....	22	.2
Antimony sulfides.....	37	.3
Fireworks.....	27	.2
Flameproofed coatings and compounds.....	316	2.6
Flameproofed textiles.....	950	7.8
Frits and ceramic enamels.....	706	5.8
Glass and pottery.....	763	6.3
Matches.....	15	.1
Paints and lacquers.....	681	5.6
Pigments.....	700	5.7
Plastics.....	620	5.1
Rubber products.....	49	.4
Other (includes antimony trichloride and sodium antimonate).....	1,969	16.2
<b>Total nonmetal products.....</b>	<b>6,855</b>	<b>56.3</b>
<b>Grand total.....</b>	<b>12,180</b>	<b>100.0%</b>

\* U. S. Bureau of Mines, 1955, Primary antimony in 1954: Mineral Industry Surveys, Mineral Market Rept. No. 2385.



## EXPLANATION

- a. roasting furnace
- b. condensers
- c. oxide collecting chambers
- d. exhausting fans
- e. cake tower
- f. water spray
- g. oxide settling pits

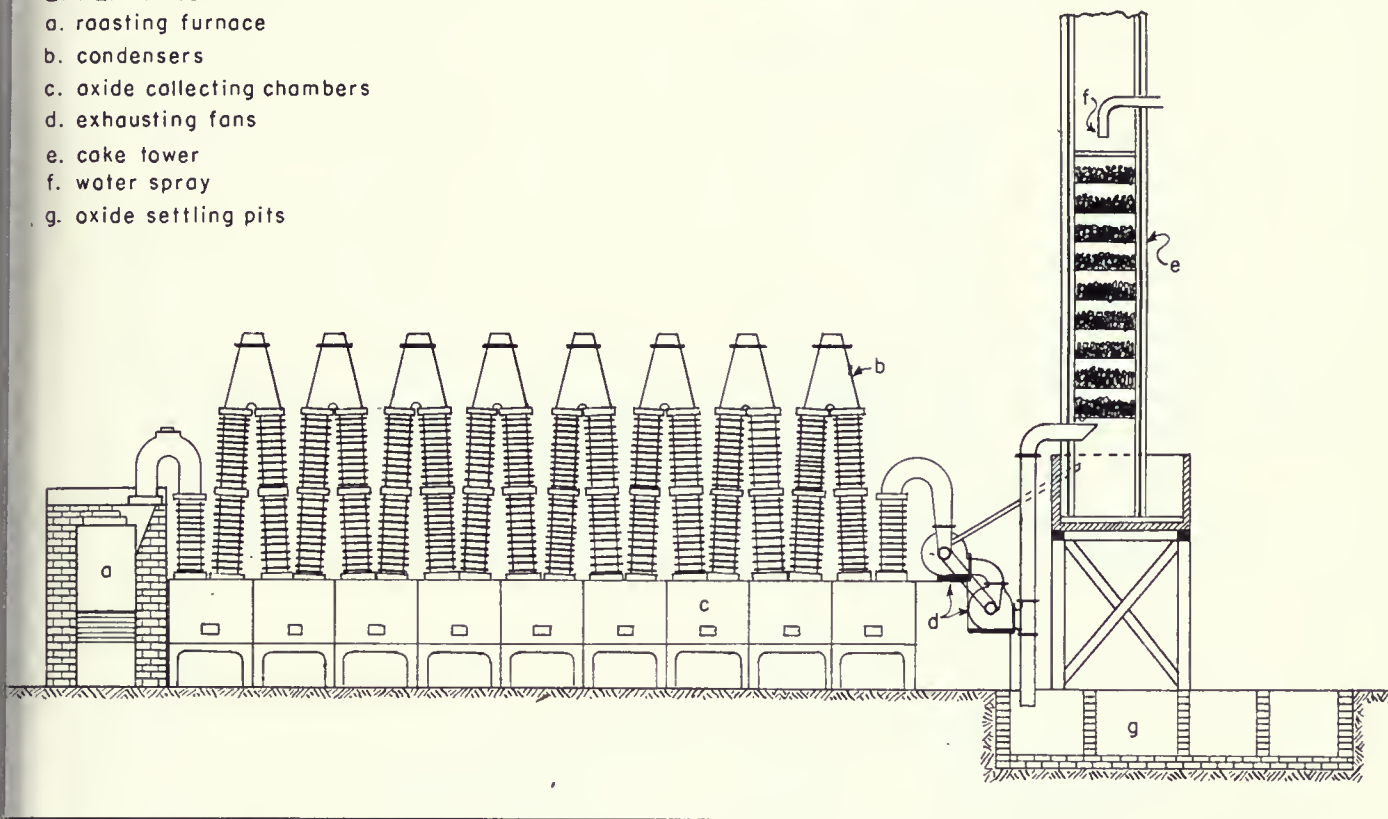


FIGURE 6. Herreschmidt roasting plans for producing antimony trioxide. After Wong, *Metallurgy of Antimony*.

Two potential applications that may ultimately require large tonnages of antimony are under development: (1) the use of antimony as a partial substitute for nickel in electroplating and (2) the use of antimony semiconductor compounds, aluminum-antimony and indium-antimony, in new types of electronic devices.

Materials that can be partially substituted for antimony include calcium as a hardening agent and bismuth in battery plates. Cadmium, titanium, and antimony are competitive pigments.

## MINING METHODS AND TREATMENT

Because most of the world's antimony ores are obtained from small irregular and scattered bodies, they have not been mined by large-scale methods. Mining is selective, is done mostly by hand, and the ore is hand sorted. The deposits have been developed by open pits or by shallow underground workings.

Most antimony-bearing ores can be successfully concentrated by combined gravity separation and flotation methods. Flotation of the simple ores (stibnite in a siliceous gangue rock) is accomplished by using standard reagents such as sodium carbonate, sodium silicate, copper sulfate, xanthate, cresylic acid, and pine oil. Complex sulfide ores have been beneficiated successfully by differential flotation at the Yellow Pine mine, Idaho. As the antimony-bearing sulfide is generally in small, disseminated grains, fine grinding is required. The mineral stibnite is soft, friable and breaks readily on grinding to produce slimes not recoverable by gravity meth-

ods. Gravity concentration, therefore, has not proved very successful in practice except as an adjunct to flotation.

Oxide ores have not been floated successfully. Hand sorting and hand jigging have been used to raise the grade of these ores for shipment.

Antimony is extracted from its ores by pyrometallurgical, hydrometallurgical or electrolytic processes, or combinations of them. The method of extraction is determined largely by the grade of ore (Dennis, 1954; Wang, 1952).

Table 2. Methods generally adopted in antimony smelting.\*

Type of ore	Approximate Sb content (percent)	Method
Sulfide.....	20	Volatilization
Sulfide.....	35	Blast-furnace method
Sulfide.....	50	Liquation and English precipitation
Oxide.....	30	Blast-furnace method
Oxide.....	50	Blast-furnace method
Oxide and sulfide.....	--	Blast-furnace method

\* Wang, C. Y., and Riddell, G. C., Antimony, in Liddell, D. M., and others, *Handbook of Nonferrous Metallurgy*, 2d ed., vol. 2, p. 137, 1945.

The pyrometallurgy of antimony is based on the ready volatility of the oxide and the ease of reducing the sulfide and oxide to metal.

In China the liquation of high-grade stibnite ores (50 percent antimony) has been a common practice. The



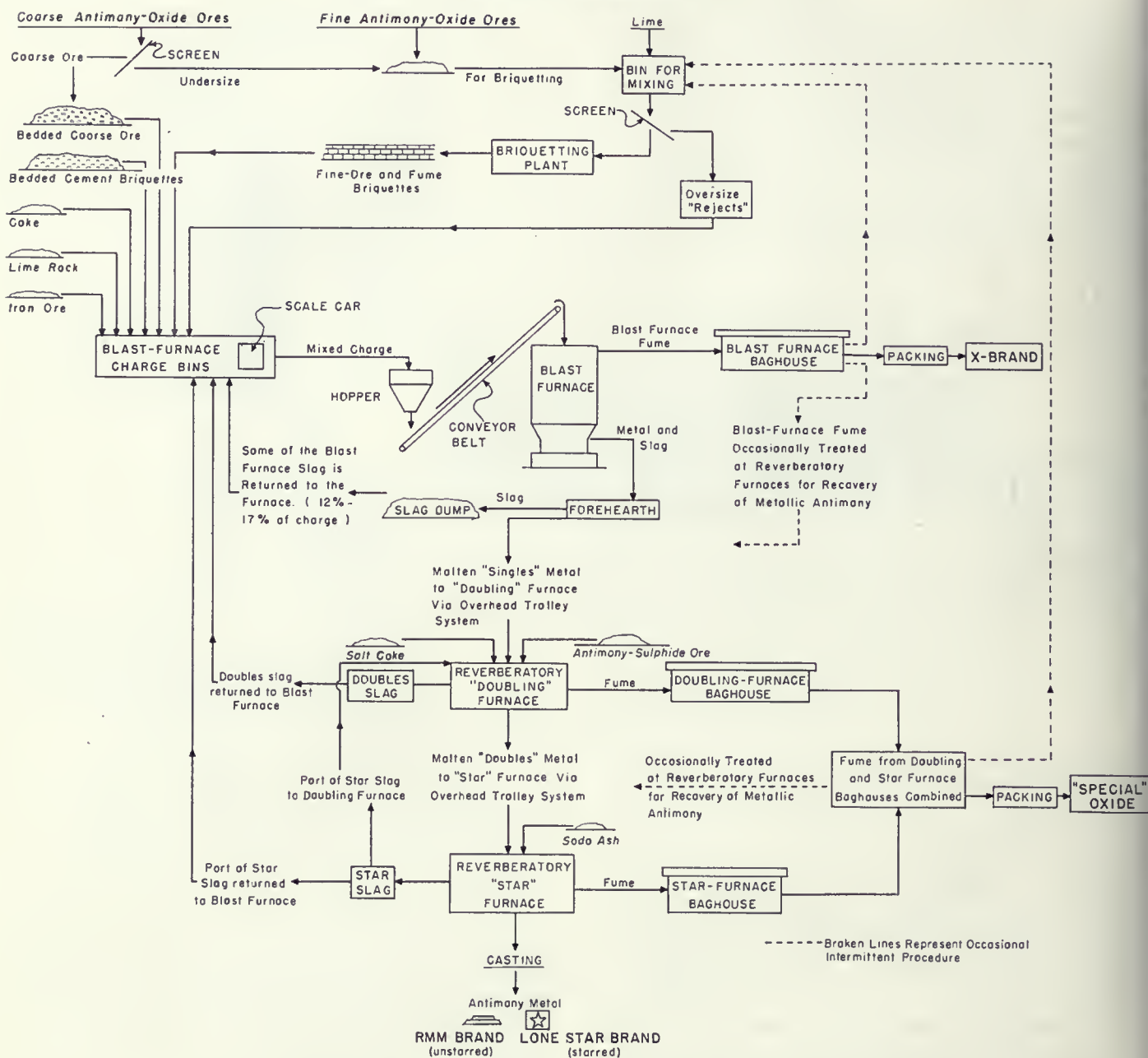


FIGURE 7. Flow sheet of Laredo antimony smelter. After *Journal of Metals*, June 1953.

process is simple and involves heating the charge just enough to permit the release of the antimony as molten material of low purity.

Sulfide concentrates of lower grades (15 to 25 percent antimony) are volatilized or roasted to produce a trioxide which may be marketed as such or reduced to metal. Processes employing volatilization as a means of extraction differ only in the types of roaster used. One of the oldest processes, the Herreshmidt, uses a grate type roaster. Fume products from these volatilization plants are collected in flues and baghouses and are reduced to metal in reverberatory furnaces.

The blast-furnace smelting of sulfide or oxide ores of antimony directly to the metal is similar in many re-

spects to the procedure for smelting lead. Actually the blast furnace is another variation of the volatilization process coupled with smelting for the production of metal. The ores most suitable for blast furnace smelting are those containing between 25 and 40 percent antimony. The blast-furnace method is used at the National Lead Company's antimony smelter at Laredo, Texas. The only antimony smelter to have been active in California was operated by the Harshaw Chemical Co. in El Segundo, Los Angeles County. This plant which was active from 1940 to 1949 occasionally purchased small lots of California ore. Their process involved flash-roasting of concentrates and reduction of the trioxide in a reverberatory furnace to an unrefined metal that was later purified.



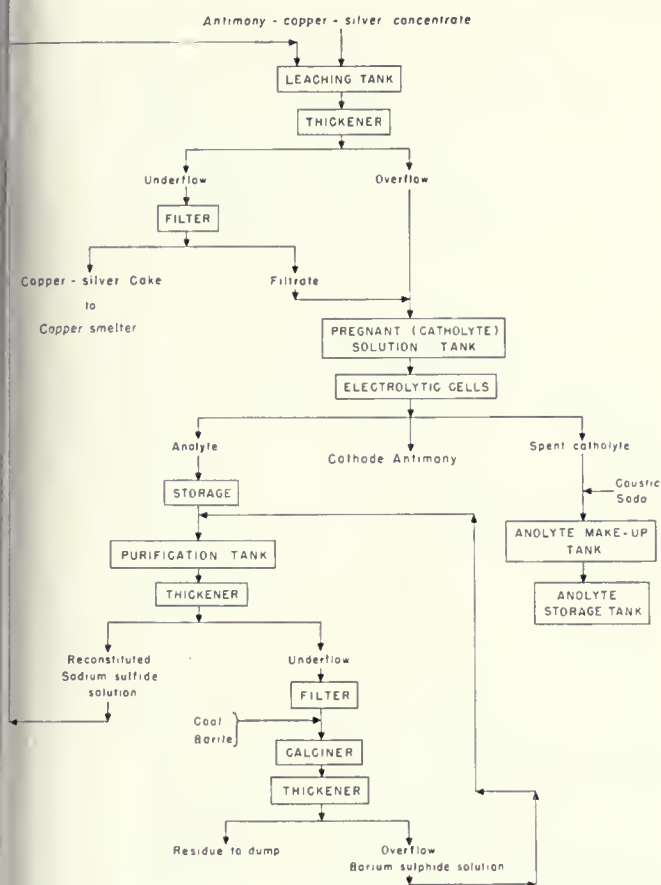


FIGURE 8. Sunshine electrolytic antimony plant. After Dennis, *Metallurgy of the Non-Ferrous Metals*.

Antimony was recovered by hydrometallurgical methods by the Sunshine Mining Company, Kellogg, Idaho from 1942 to 1944, and the Bunker Hill and Sullivan Mining and Concentrating Company, Kellogg, Idaho from 1940 to 1950. In both cases the ore was tetrahydrite, a complex silver-copper-antimony sulfide containing 20 percent antimony. The process involved leaching the concentrate with a hot sodium sulfide solution to dissolve out the antimony. The solution was then treated by electrolysis and the antimony precipitated on mild-steel cathodes. Both electrolysis plants are shut down.

Metal produced by many of these methods is impure; it is termed crude or unrefined antimony, and must be treated to remove the objectionable impurities such as arsenic, iron and other metallic components. Lead is difficult to remove and consequently antimony ores or crude metal that contain a significant amount of lead commonly are converted to antimonial lead or hard lead for the trade. Electrolytic methods as well as reverberatory furnace methods are used to refine impure antimony. The refined metal is cast so that the surface has a "starred" appearance. This surface is obtained by using a refining flux that remains molten at a temperature below the solidification point of the metal. The metal solidifies under the molten cover enabling the surface crystals to assume a dendritic form.

Table 3. Annual tonnage and value of antimony produced in California 1887-1954.<sup>1</sup>

Year	Tons <sup>2</sup>	Value	Year	Tons	Value	Year	Tons	Value
1887	75	\$15,500	1902	510	35,666	1943	0	0
1888	100	20,000	1916	1,015	64,793	1944	3½	600
1889	0	0	1917	158	18,786	1948	2	1,467
1893	50	2,250	1918	0	0	1952	7 <sup>3</sup>	--
1894	150	6,000	1925-26	26	770	1953	2 <sup>3</sup>	--
1895	33	1,485	1927	20	590	1954	0	0
1896	17	2,320	1928	20	761			
1897	20	3,500	1929	0	0			
1898	40	1,200	1939	150	4,552			
1899	75	13,500	1940	28	7,958			
1900	70	5,700	1941	10	2,537			
1901	50	8,350	1942	30	9,251			

<sup>1</sup> After C. V. Averill and others, 1948, California mineral production for 1946: California Div. Mines Bull. 139, p. 32.

<sup>2</sup> Tonnage figures 1889-1939, inclusive, represent tons of antimony ores shipped 1940-51 amount of recoverable metal. To conceal output of individual producers where necessary, production figures are omitted or combined to cover a 2-year period.

<sup>3</sup> Ore mined but not shipped.

### MARKETS AND PRICES

Because of the lack of tariff protection, domestic producers have been unable to compete with low-cost imports, and in 1952 the Yellow Pine mine in Idaho shut down (Rennick and Wright, 1955, p. 151). As the foreign producers have richer natural deposits and much lower labor costs, the domestic output of antimony has been very small since 1952. In 1954, domestic antimony production totaled approximately 800 tons of

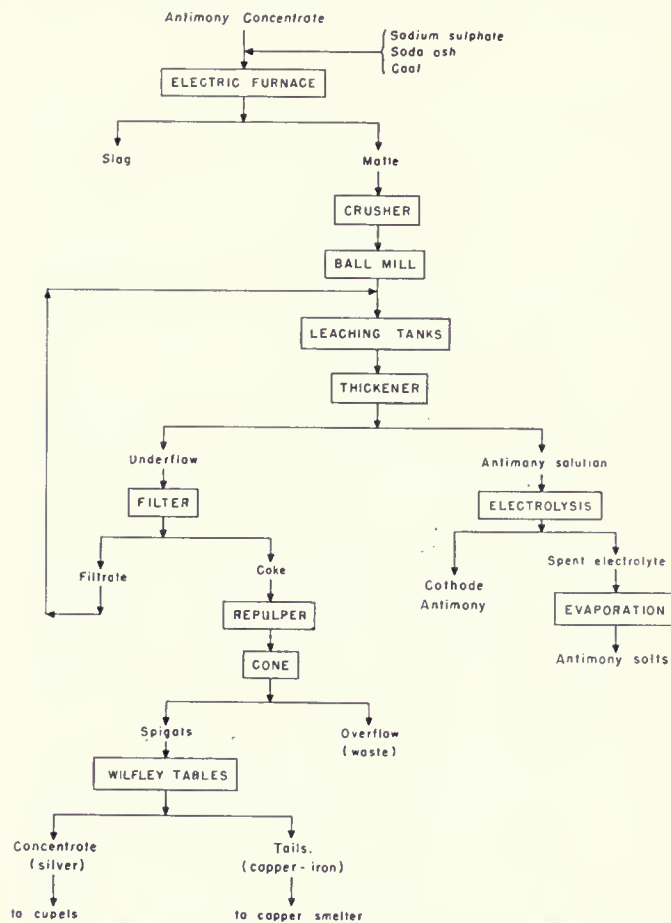


FIGURE 9. Bunker Hill and Sullivan electrolytic plant. After Dennis, *Metallurgy of the Non-Ferrous Metals*.





FIGURE 10. Refined "starred" antimony metal.  
Photo by Mary Hill.

metal obtained principally as the by-product of complex lead-silver-copper ore.

In 1955, the industrial consumption of primary antimony in the United States in both metallic and nonmetallic products totaled 12,500 tons, a 2 percent increase over 1954.

Domestic primary antimony smelters produced 8200 short tons of metal, oxide and sulfide in 1955, an increase of 3 percent over 1954. Domestic primary lead smelters produced 2200 short tons of antimonial lead as a by-product from domestic and foreign silver and lead ores. The total production of antimony at secondary smelters was estimated at about 21,000 short tons. In 1955 imports of ore oxide, and metal chiefly from Mexico, Bolivia, Union of South Africa, and Belgium-Luxembourg, totaled 13,000 tons of contained antimony (U. S. Bureau of Mines, 1955 Mineral Market Report M.M.S. 2501).

The price of antimony metal as of May 1956 was quoted at 33.0 cents per pound bulk, Laredo, Texas. Nominal quotations for ore containing a minimum grade of 50 to 55 percent antimony was \$3.20 to \$3.35 per short ton unit (\$160 to \$184 per ton of ore). Antimony prices are characterized by relative instability and wide fluctuation. During wartime, demand increases greatly because of military uses; during depression demand decreases considerably. Because of price uncertainty operators are reluctant to make capital commitments for mechanization. Domestic reserves are small and low grade and because of high labor costs can not be worked without mechanization.

At the Western Governors Mineral Policies Conference, held in Sacramento in November 1955, the conference committee on antimony agreed that the reactivation of some of the larger antimony deposits in California would require that the price of the ore and concentrate (45 percent antimony or better) be raised to at least 30¢ per pound of contained antimony and that the price of the smelted products (metal and oxide) be raised to 60¢ a pound. Such an increase in price for the ore and concentrate would probably put into operation

those California deposits that contain ores averaging 3 percent or more antimony. Under the present (1956) price of \$3.20 per unit (for 50 percent antimony concentrate), the California producer probably could not work economically deposits that average less than 6 percent antimony. The nearest antimony smelter is at Laredo, Texas. The cost of shipping antimony ore from any point in California to Laredo is \$26.54 per ton for a 40-ton minimum carload or \$31.50 per ton for a 30-ton minimum carload.

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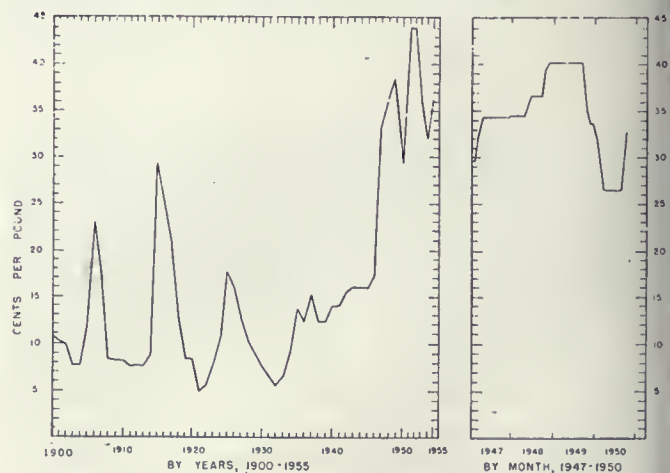


FIGURE 11. Antimony prices, 1900-55, f.o.b. New York. After U.S. Bur. Mines and U.S. Geol. Survey, Antimony, Materials Survey.



## ARSENIC

By J. GRANT GOODWIN

Though arsenic is not an abundant element, it is widely distributed in the earth's crust. Arsenical ores of lead, copper, silver, and gold are common in California and throughout the western United States and Mexico. The domestic supply would be more than adequate to meet demand if the price paid for arsenic was sufficient to encourage recovery. Arsenic is considered a nuisance by refineries because of its deleterious effects and arsenical ores are penalized heavily. It is recovered principally as a matter of necessity in the smelting and refining of other ores. Arsenic therefore is a by-product metal not sought after and ordinarily avoided whenever possible. Sweden alone unavoidably produces more arsenic each year at the Boliden copper mine than the world is consuming annually. Arsenic from California ores and smelter residues is ultimately recovered along with other by-product metals at scavenger smelters in the western United States. Most of the arsenic of industry is white arsenic (arsenic trioxide) of value principally because of its toxic properties. The principal use for white arsenic is in the manufacture of insecticides and herbicides.

*Arsenic in Nature.* The principal arsenic minerals are arsenopyrite or mispickel (sulfarsenide of iron), löllingite (iron arsenide), enargite and tennantite (sulfarsenides of copper), realgar and orpiment (arsenic sulfides), and the arsenides of nickel and cobalt. Native arsenic is known but rare. A large number of less common sulfarsenides of the metals are known. Arsenopyrite is by far the principal source of white arsenic in industry. Arsenic-bearing minerals are common in many ores of the base and precious metals. Notable examples of high-arsenic ores are: (1) arsenopyrite-bearing copper ore at Boliden, Sweden; (2) enargite-bearing copper ore at Butte, Montana; (3) arsenic-bearing copper-lead-silver ores of Mexico; (4) arsenopyrite-bearing gold-silver-lead ores of Nevada; (5) arsenopyrite-bearing silver ores in the Randsburg district, California; and (6) arsenopyrite-bearing gold ores of the Alleghany district, California.

*Properties of Arsenic.* Arsenic is a gray metal with a metallic luster. It has a specific gravity of 5.6 to 5.9, a hardness of 3.5 (Mohs' scale), and is extremely brittle. Arsenic will melt at red heat under pressure and in the absence of oxygen; at atmospheric pressure, however, it passes from a solid to a gas at a temperature of 450° C. Arsenic acts as both a metal and nonmetal, by forming oxides or combining with metals to form arsenides. It has a valence of 3 and 5. Arsenic burns in air, giving off dense white fumes of arsenous oxide which may be recognized by their characteristic garlic odor. The physical and chemical properties of arsenic render it worthless as a structural metal. The fact that small amounts of arsenic impart brittleness to metals limits its use in alloys. The principal commercial use of arsenic is in insecticides and herbicides where the toxic nature of arsenical compounds is utilized.

*Recovery of Arsenic.* The arsenic of industry is recovered largely as arsenic fume (impure arsenous tri-

oxide from smelter stacks, Cottrell dust precipitators, and baghouse dusts). Lead baghouse dust and copper furnace and roaster dusts commonly contain from 20 to 30 percent arsenic which is in the form of arsenous trioxide. This dust is revolatilized in reverberatory furnaces and sublimed in the cooling chambers of arsenical kitchens as pure white arsenous trioxide, the arsenic of industry. This is by far the greatest source of arsenic. At lead smelters a copper-iron speiss containing about 30 percent arsenic and variable quantities of lead, nickel, and other metals is separated from the lead bullion. The speiss is shipped to copper smelters for recovery of the copper and other metals. Drosses skimmed from the softening kettles at lead refineries, composed largely of arsenides and antimonides, are refined at scavenger smelters for recovery of the contained metals. Arsenic is also recovered from the electrolytic baths at copper refineries where it is precipitated as calcium arsenate and sold directly as an insecticide.

*Arsenic in California and the History of Arsenic in the United States.* Arsenic occurs in California principally in the mineral arsenopyrite, which is widely distributed. As previously noted, it is especially abundant in the arsenopyrite-bearing silver ores of the Randsburg district, and in the arsenopyrite-bearing gold ores of the Alleghany district and the Mother Lode. Arsenopyrite and sulfarsenides also are present in the base-metal ores of the Mojave Desert, Sierra Nevada foothills, and Shasta district. At only three localities has there been any attempt to mine arsenical-bearing vein material principally for its arsenic content. In 1920, ore containing 12 to 14 percent arsenic was shipped from the Sultana mine near Grass Valley to the Tacoma smelter in Washington (Heikes, 1922).

In November, 1923, Arsenic Products and Refining Company, owned by Chipman Chemical Engineering Company, converted the Butters cyanidation plant at Martinez, California, into an arsenic plant. The company's principal source of ore was from Nevada, but in 1924 they solicited California ores and received about 35 tons of ore containing 15.8 percent arsenic from the Contact mine northwest of Rosamond in Kern County. The ore was shipped from Kernville by Oliver Hitchcock. During the same year an attempt was made to recover crude arsenic fume from the arsenopyrite-bearing veins at the Black Mountain prospect southeast of Escondido in San Diego County. Only 700 pounds of crude arsenic fume containing 31.4 percent arsenic was produced; this was shipped to Arsenic Products and Refining Company by Frank Chopkins of Escondido. The operation was subsequently abandoned. Arsenic Products and Refining Company consumed their output of white arsenic in the manufacture of a herbicide, then in great demand by the railroads for weed killing along right-of-ways. During the same period National Chemical Company at Pittsburg, California, also produced arsenical compounds. The arsenic industry was short-lived and in 1925 both plants were closed and dismantled (Ambruster, 1926).

Dry weather which kept weeds and insects under control caused a drop in demand for insecticides and herbi-



cides. The price of white arsenic dropped from 13½ cents per pound to 6½ cents per pound during 1924 and has remained at or below that level up to the present time. At this price, arsenic production has been unprofitable and arsenic has thus assumed the role of a troublesome and unwanted by-product.

Heikes (1923) states that California probably ranked sixth in the United States in the production of arsenic in 1922. The source of this arsenic was the copper-iron-arsenic speiss shipped to Tacoma, Washington, from the copper smelters at Copperopolis and in the Shasta district, from copper concentrates and ores shipped to Tacoma from the Sierra Nevada foothill belt and Shasta district and from arsenical silver ore shipped from the Randsburg district. California's production of arsenic from these sources dates back to 1901 when the first recovery of arsenic in the United States was made by Puget Sound Reduction Company, at Everett, Washington (Struthers, 1902). This smelter, owned by American Smelting and Refining Company, was treating copper speiss and copper ores and concentrates from the western United States. Prior to 1901 the entire United States arsenic supply was imported.

By 1905, Anaconda Company had installed arsenical kitchens and was recovering white arsenic at Butte, Montana. Other western smelters later installed recovery units and arsenic kitchens to supply the increasing demand for arsenic by agriculture until, by 1924, nine smelters in the United States were producing white arsenic. The low price of arsenic since 1924 which resulted from oversupply and decreasing demand closed many of the arsenic plants and forced arsenic to assume its by-product role. During the same year large quantities of by-product arsenic became available from American Smelting and Refining Company's smelter in Mexico.

The arsenic content of most base-metal ores is below 1 percent; however, arsenical dusts and residues accumulate rapidly at the smelters. American Smelting and Refining Company's smelter at Selby, California, treats lead ores and concentrates, and gold-silver ores and concentrates from Australia, South America, and western North America. Part of the arsenic contained in the ores is volatilized and caught by the Cottrell electrostatic precipitators and in the bag house. The bulk of the remainder forms a copper-iron-arsenic speiss which separates from the slag and from the lead bullion. The remainder of the arsenic (and antimony) is removed as a dross from lead bullion during the process of softening. The dross and flue dusts were formerly shipped to the Murray smelter in Utah, which acted as a scavenger smelter. The copper-iron speiss from Selby is shipped to the Tacoma copper smelter where by-product arsenic is produced. Arsenic from California ores and concentrates has also been recovered at the Anaconda smelter in Montana, at the Midvale, Utah, smelter owned by United States Smelting, Refining and Mining Company, and at the El Paso smelter operated by American Smelting and Refining Company. Statistics are not available on total production of arsenic from ores mined in California.

The production of white arsenic in the United States began in 1901 when Puget Sound Reduction Company produced the first 300 tons. Production and consumption increased rapidly until 1924 when 20,177 short tons were produced and 24,000 tons were consumed. Domestic pro-

duction did not reach this level again until the World War II period when it reached an average of 28,000 short tons annually. The peak year was 1944 when 36,094 tons of white arsenic was produced. During 1942 the consumption of white arsenic was at an all-time high of 47,083 short tons. Exclusive of the war years the average annual consumption of white arsenic in the United States has been about 24,000 short tons, about 50 percent of which has been imported, mainly from Mexico. In 1953 domestic production of white arsenic dropped to 10,873 short tons and the apparent consumption dropped to 16,032 short tons. All of the metallic arsenic that is consumed domestically is imported. This totals only about 100 to 125 short tons a year and is consumed in hardening lead and in special copper alloys (Renick, 1955). Smelters in the United States have a potential capacity of more than 30,000 short tons of white arsenic annually if the need should arise. The estimated domestic reserves of white arsenic are 2½ million short tons (Renick, 1955).

*Marketing of White Arsenic and Arsenic Compounds in California.* The white arsenic of industry is sold to manufacturers of insecticides and herbicides who prepare the arsenical compounds marketed as toxants. In California, Federated Metals, a marketing division of American Smelting and Refining Company, is the principal wholesale outlet for white arsenic. It is sold in carload lots only. The various chemical supply houses act as wholesalers and retailers of smaller lots.

The annual consumption of white arsenic by the insecticide-herbicide industry in California in recent years is estimated to be about 2,000 short tons. California Spray-Chemical Corporation is the largest consumer.

*Uses of Arsenic.* The principal uses for white arsenic are in the preparation of herbicides, wood preservatives, and insecticides, and in the manufacture of glass. In 1953 an estimated 50 percent of the total white arsenic consumption was in the manufacture of herbicides and wood preservatives, 40 percent in the manufacture of insecticides, and 10 percent in the manufacture of glass (Renick, 1955). The principal toxic compounds are: (1) basic lead arsenate sprays and dusts used chiefly for destroying the codling moth and various chewing insects; (2) tri-calcium arsenate, used chiefly for boll weevil control and snail bait; (3) sodium arsenite, used chiefly as a herbicide and also in ant poisons, termite controls, cattle dip, chemical debarking of trees in the pulpwood industry, and in defoliants for cotton and other crops; (4) arsenic trioxide solutions, used in wood preservatives and soil sterilization; and (5) basic copper arsenate or Paris Green, used against chewing insects. In the glass industry (Weyl, 1951), arsenic is used: (1) in soda-lime-silica glass where from 0.3 to 0.5 percent arsenic trioxide is used as an oxidant of small concentrations of iron; (2) with manganese where the equilibrium between  $As_2O_3$  and  $As_2O_5$  acts as an oxygen buffer to the sensitivity of the  $Mn_2O_3$  equilibrium during local or temporary changes in the oxidation-reduction condition of the furnace atmosphere; (3) in the refining of selenium pink glass, also as an oxygen buffer; and (4) in phosphate glasses for high ultra-violet transmission.

The minor uses for arsenic include the use of metallic arsenic: (1) to harden lead in the lead shot industry; (2) in special copper alloys; (3) in solder where arsenic



*Principal producers and distributors of arsenical compounds in California.*

<i>Company</i>	<i>Product</i>	<i>Active ingredient</i>
California Spray-Chemical Corp. Richmond, Calif.	Ortho Basic Lead Arsenate Meta Agricultural Bait Ant-B-Gon Sodite Arsenical Poison Triox	lead arsenate tri-calcium arsenate sodium arsenate arsenic trioxide sodium arsenite
A. L. Castle, Inc. Mountain View, Calif.	Castle Meta-Pellets	tri-calcium arsenate
Chipman Chemical Co., Inc. Palo Alto, Calif.	Atlas A. Sodium Arsenite Solution	sodium arsenite
Fresno Agricultural Chemical Co. Fresno, Calif.	Red Top Arsenate Dust 50	tri-calcium arsenate
Los Angeles Chemical Co. Los Angeles, Calif.	Lacco Mono Calcium Arsenate Lacco Sodium Arsenite Solution No. 4	mono calcium meta-arsenate arsenic trioxide
Niagara Chemical Division Food Machinery & Chemical Corp. Richmond, Calif.	Niagara Standard Lead Arsenate	lead arsenate
Pacific Guano Company Berkeley, Calif.	Agricultural Taps	tri-calcium arsenate
Sherwin-Williams Co. Oakland, Calif.	Basic Copper Arsenate	copper arsenate
Stauffer Chemical Co. San Francisco, Calif.	Sulfur-lead Arsenate Dust 50-50 Cal-Meta Pomace Snail Bait Calcium Arsenate Dust Mixture	lead arsenate tri-calcium arsenate tri-calcium arsenate
United Chemical Co. Richmond, Calif.	Sodium Arsenite Solution	arsenic trioxide
Westside Products Co. Newman, Calif.	Westside B-S Bait	tri-calcium arsenate

may partially substitute for tin; and (4) in lead-base alloys for battery grids, bearings, cable coverings, and anodes used in zinc electrolysis. The proportion of arsenic used in these alloys is normally less than 1 percent. Three commercial sulfides of arsenic are also known. Arsenic disulfide is used as an orange pigment, a depilatory in tanning, and in pyrotechnics. Arsenic trisulfide is used as a yellow pigment (king's yellow) and as a reducing agent. Arsenic penta-sulfide has limited use in pigments and in pyrotechnics. Minor arsenic and arsenical compounds are also used in pharmaceuticals.

*Trend and Outlook.* The recent trend away from the use of arsenical compounds in agriculture has greatly reduced the market for white arsenic. Calcium arsenate is being rapidly replaced by a DDT-benzine hexachloride dust in the control of the cotton boll weevil, and sodium arsenate is being replaced by 2,4-D as a herbicide. Lead arsenate is still favored by many for orchard use against the codling moth because DDT also destroys many useful insects. The demand for arsenical compounds cannot be predicted because weather conditions directly control the insect population. Arsenicals will continue to play an important role as a pesticide; however, the demand may be cyclical. Some insects develop an immunity to certain poisons over a period of years, therefore it may be necessary to rotate regularly the type of poison used. The use of sodium arsenite solution in the chemical debarking of trees by the pulpwood industry may develop into an important new outlet for arsenic (Jahn, 1953). Sodium arsenite has also been used with good results in controlling aquatic plants in swamps, ponds, and lakes, and there is a large potential market in this field.

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## ASBESTOS

By SALEM J. RICE

Asbestos is one of the few industrial mineral commodities in which the United States is critically deficient. Although certain grades of asbestos are indispensable to our transportation and construction industries, and all grades occupy an important place in our normal industrial economy, only about seven percent of our requirements are supplied from domestic sources. Most of the remaining 93 percent is obtained from Canada.

California contains abundant serpentine, the principal host rock of asbestos deposits, and asbestos has been found in numerous places in the state. However, known deposits of potential commercial interest are rare and the production of asbestos in the state has been small and sporadic. Between 1887 and 1955, approximately 5,700 tons of asbestos, valued at an estimated \$218,000, had been produced in the state.

### MINERALOGY AND GEOLOGIC OCCURRENCE

Asbestos is a commercial term applied to several naturally fibrous minerals that are utilized primarily because of their fibrous characteristics. These minerals include chrysotile, crocidolite, amosite, anthophyllite, tremolite, and actinolite. As these minerals differ in chemical and physical properties, and have different modes of occurrence, they will be discussed separately.

**Chrysotile Asbestos.** Chrysotile ( $H_4Mg_3Si_2O_{10}$ ), sometimes called serpentine asbestos, comprises about 95 percent of the world's asbestos production. Chrysotile fibers of good quality are silky, highly flexible, and have a tensile strength somewhat greater than that of silk. Thus they can be readily separated and spun into thread that is sufficiently strong to be woven. In the vein, chrysotile appears pale green to greenish yellow, but when separated the fibers form a white, fluffy mass. Chrysotile occurs most commonly as cross fiber veins, ranging in width from microscopic dimensions to more than 6 inches, in which the fibers lie approximately perpendicular to the walls. The vein widths, however, are not everywhere indicative of the maximum lengths of fiber that they contain, for most of the wider veins have a central fissure or break along which the fibers separate.

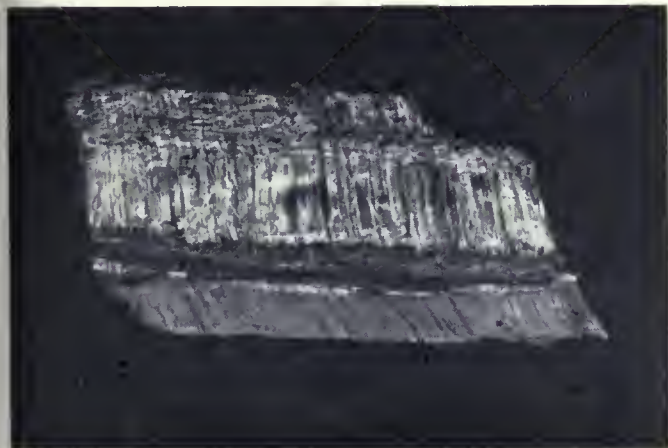


FIGURE 1. Composite vein showing silky cross-fiber chrysotile above and dull splintery picrolite below.



FIGURE 2. Typical appearance of stockwork veins of cross-fiber chrysotile asbestos in massive serpentine.

The only mineral likely to be mistaken for chrysotile is picrolite, a splintery vein material. The two are similar in composition and appearance, and commonly occur together in composite veins (fig. 1). However, picrolite does not yield flexible fibers and has no commercial value.

Chrysotile occurs only in serpentine, a fine-grained rock composed almost entirely of hydrous magnesium silicate minerals that are similar to chrysotile in chemical composition (Nagy and Faust, 1956). Serpentine is a secondary rock, derived by alteration of other magnesium-rich rocks. Almost all of the valuable deposits of chrysotile occur in massive serpentine derived by the alteration of peridotite, an intrusive igneous rock composed largely of olivine and pyroxenes. Many peridotite masses are entirely altered to serpentine, and all but a very small percentage of them are at least partially serpentinized. Cracks formed by differential expansion of the rock during serpentinization commonly were filled with chrysotile. The resulting veins ordinarily are less



than one-sixteenth of an inch wide and rarely are more than one inch wide.

Individual chrysotile veins seldom are continuous for more than a few feet, but they pinch out, branch, or join other veins. Many thin veinlets are less than an inch long. In most deposits the veins form a somewhat rectilinear stockwork that encloses blocks of barren serpentine (fig. 2). This is true of most of the productive chrysotile deposits. A rare type contains "ribbon veins" which are closely spaced and sub-parallel, and are separated only by thin plates of serpentine. Ribbon veins normally occupy narrow zones from a few inches to a few feet wide, but some are extensive and constitute rich asbestos ore bodies.

Some chrysotile veins, which lie along faults or minor slip planes between blocks of massive serpentine, contain fibers that lie approximately parallel to the fissure, and are called slip fiber veins. Although slip fiber chrysotile is longer than most cross fiber, normally it is weaker and more harsh. In most places slip fiber is of little commercial value, but in a few mines it constitutes a substantial proportion of the asbestos produced (Bowles, 1955).

Chrysotile veins can be found in all masses of serpentinized peridotite, but rarely are they sufficiently abundant to constitute asbestos ore bodies. About 70 percent of the world production of chrysotile comes from a relatively small district in the province of Quebec, Canada, where a northeast-trending belt of serpentinized peridotite contains many rich asbestos deposits. The discovery of these deposits in 1877 laid the foundation of the modern asbestos industry. Substantial amounts of chrysotile also are produced from similar deposits in Southern Rhodesia, Transvaal, and Swaziland (Straw, 1955).

The asbestos deposits in Quebec are large, and commonly irregular in shape. The Thetford ore body is pear shaped in plan, and is about 2200 feet long and 1300 feet in maximum width. Asbestos is now being mined deeper than 1000 feet below the surface and the maximum depth of the body is unknown (Sherman, 1950). Three companies have mines in this deposit, and in 1955 were producing a total of about 8600 tons of ore per day. The Megantic ore body at Black Lake is hook-shaped in plan, and is approximately 4000 feet long, 700 feet wide, and 300 feet deep (Mining World, 1955). The main ore body at Asbestos, Quebec, is cylindrical and plunges steeply to the southwest. It is about 2700 feet in maximum horizontal dimensions and extends to a depth greater than 1000 feet (Briggs, 1955). This is the largest known asbestos deposit in the world.

Most of the ore bodies in Quebec contain 5 to 7 percent fiber, although at some deposits rock that contains as little as  $1\frac{1}{2}$  or 2 percent fiber is worked (Messel, 1947). The veins are irregularly distributed within the deposits, so that normally about 20 percent or more of the rock mined is barren and discarded as waste. Consequently, the mill feed at most of the mines contains  $7\frac{1}{2}$  to 8 percent fiber. More than 99 percent of all the veins are less than three-eighths of an inch wide, and veins wider than  $1\frac{1}{2}$  inches are rare (Cooke, 1937, p. 91).

In general, the potential commercial value of a chrysotile deposit in massive serpentine is determined by balancing a number of factors, principally the fiber content of the rock, proportions of the various fiber lengths,

and volume of fiber-bearing rock. The fiber content of the rock, which depends upon both the width and spacing of the veins, seldom exceeds 5 percent. The bulk of the fiber in most of the world's deposits is less than a quarter of an inch long, and is therefore of relatively low value. Further, the clean extraction of the fiber from the serpentine is a highly complicated process, involving a costly milling procedure. Thus a deposit generally must be sufficiently extensive to sustain a large-tonnage, low-cost mining operation over a period of at least 10 to 20 years in order to yield a profit. Ordinarily exploration by diamond drilling is necessary in order to establish the required tonnage (Messel, 1947; Foster and Borror, 1947). Local concentrations of long fiber veins that can be freed from the country rock by hand cobbing support a few small mining operations, but these yield only an extremely small percentage of the total chrysotile asbestos produced.

Aside from its principal occurrence as a massive alteration product of peridotite, serpentine also occurs locally as thin alteration zones in dolomite or dolomitic limestone along contacts with intrusive basic igneous rocks. These serpentine zones range in thickness from a few inches to about 5 feet. In places chrysotile of excellent quality is found in this environment, one or more veins occurring approximately parallel to the intrusive contact. Because of the narrow width of the productive zones and the high costs of mining them, deposits of this type are of value only where long fiber chrysotile is found. Almost the entire U. S. production of long fiber chrysotile comes from such deposits in Arizona (Stewart, 1955).

Chrysotile is one of the strategic minerals for which exploration loans may be obtained from the U. S. Defense Minerals Exploration Administration. As the critical shortage is in the textile grades, only those prospects are eligible which show promise of yielding spinning fiber. After an asbestos prospect has been approved for such a loan the Government will pay 75 percent of the cost of exploration. Through 1955, a total of five exploration loans had been approved for California chrysotile deposits. The amphibole varieties of asbestos are not eligible for these loans.

*Amphibole Asbestos.* All varieties of asbestos other than chrysotile are members of the amphibole group of minerals, and are collectively called amphibole asbestos. The amphiboles are an exceedingly common group of rock-forming minerals characterized by perfect prismatic cleavage with angles of  $56^\circ$  and  $124^\circ$  between the cleavage planes. Included in the group are several isomorphous series of complex silicate minerals. Only a few of these minerals, principally those that are aluminum-poor, occur in asbestiform masses.

Tremolite ( $\text{Ca}_2\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$ ), the most common variety of amphibole asbestos, has coarser and much weaker fibers than those of chrysotile. A bundle of tremolite fibers the diameter of a match stick can easily be broken between the fingers, whereas a similar bundle of chrysotile fibers cannot be broken without considerable flexing. Tremolite asbestos occurs most commonly as slip fiber veins in fault zones. The fibers are white to greenish white and are as much as a foot or more in length (fig. 3). It is found in a variety of host rocks,





FIGURE 3. Slip-fiber tremolite asbestos.

both igneous and metamorphic, although most of the commercial deposits are in serpentine. Ordinarily the deposit consists of a single steeply dipping vein from which the fiber of good quality is hand sorted for sale without milling. Although most of the veins are a few inches wide and less than 100 feet long, some contain pockets up to several feet in width. They are seldom mined to depths greater than 25 or 50 feet because of the high mining costs and the relatively low value of the fiber. Tremolite asbestos accounts for less than one quarter of one percent of the total asbestos production. The principal sources are Italy, Portugal, and the United States.

Actinolite is similar to tremolite, containing iron in substitution for some of the magnesium in the composition. Actinolite asbestos is green, with fibers that are very harsh, weak, and somewhat brittle. It is similar to tremolite in occurrence, and is of little commercial significance.

Crocidolite ( $\text{Na}_6\text{Fe}_{10}\text{Si}_{16}\text{O}_{46}(\text{OH})_2$ ), a blue amphibole asbestos of considerable commercial importance, is the fibrous form of the mineral riebeckite. Its fibers are flexible and stronger than those of chrysotile, although somewhat harsher. Crocidolite occurs as cross fiber veins in metamorphosed thin-bedded sedimentary rocks that

are rich in silica and iron (du Toit, 1945). The veins are parallel to the original bedding of the rocks, and are commonly several inches wide. However, they are not closely spaced in the rock, but normally occur only in two or three narrow zones so widely separated as to make large-scale mining impractical. The principal source of crocidolite is the Union of South Africa, but lesser amounts are produced in Australia and Bolivia.

Amosite ( $(\text{Fe}, \text{Mg})_7\text{Si}_8\text{O}_{22}(\text{OH})_2$ ) is a yellowish-gray to white variety of asbestos found only in Transvaal, South Africa. It occurs in isolated cross fiber veins in the same host rocks as crocidolite asbestos. The fibers of amosite are unusually long, up to 10 or 11 inches, but are harsher and ordinarily slightly weaker than those of chrysotile. Montasite is a local name used at some of the mines in South Africa to designate amosite of superior quality.

Anthophyllite asbestos ( $\text{Mg}_7\text{Si}_8\text{O}_{22}(\text{OH})_2$ ) most commonly occurs in relatively pure masses. The fibers have no preferred orientation, but are arranged in bundles of varying sizes which are oriented in all directions with respect to each other. Unweathered anthophyllite is greenish gray to gray, and yields brittle fibers when crushed. However, when deeply weathered it yields brownish-white fibers that are short, weak, and slightly flexible. Deposits of this type of asbestos are of commercial value only when they are sufficiently large and pure to be mined and milled cheaply. The principal sources of anthophyllite asbestos are Georgia and North Carolina, where large deposits were formed through metamorphism of peridotite. The deposits in Georgia are pod-shaped masses up to about 200 feet long and 50 feet wide and consist of 90 to 95 percent anthophyllite. Although the fibers average about half an inch in length, their lack of flexibility causes them to be reduced in milling to an average length of about one-tenth of an inch (Hopkins, 1914). An unusual soda-rich anthophyllite, with fibers nearly as strong and flexible as those of chrysotile, has been found in small amounts in California (Laudermilk and Woodford, 1930).

#### LOCALITIES IN CALIFORNIA

Although asbestos has been found in nearly all of the counties of California, production has been small and

Table 1. Asbestos production in California, 1887-1955.

Year	Short tons	Value	Year	Short tons	Value	Year	Short tons	Value
1887	30	\$1,800	1910	200	\$20,000	1929	219	\$6,175
1888	30	1,800	1911	125	500	1930		
1889	30	1,800	1912	90	2,700	1932		
1890	71	4,260	1913	47	1,175	1933	309	3,274
1891	66	3,960	1914	51	1,530	1934		
1892	30	1,830	1915	143	2,860	1941	16	2,867
1893	50	2,500	1916	145	2,380	1942	4	836
1894	50	2,250	1917	136	10,225	1943	723	15,000
1895	25	1,000	1918	229	9,903	1944		
1898	10	200	1919	131	6,240	1945	37	3,605
1899	30	750	1920			1946		
1900	50	1,250	1921	410	19,275	1947		
1901	110	4,400	1922	50	1,800	1950	165	12,100
1904	10	162	1923	20	200	1951		
1905	112	2,625	1924	70	4,750	1953	224	16,779
1906	70	3,500	1925	25	1,650	1954		
1907	70	3,500	1926			1955	1,205	21,401
1908	70	6,100	1927	13	1,160	Modified after Averill et al., 1948, p. 60.		
1909	65	6,500	1928					

NOTE: Where necessary in order to conceal output of individual producers, production figures are combined to cover a 2- or 3-year period. During years omitted there was no recorded production.



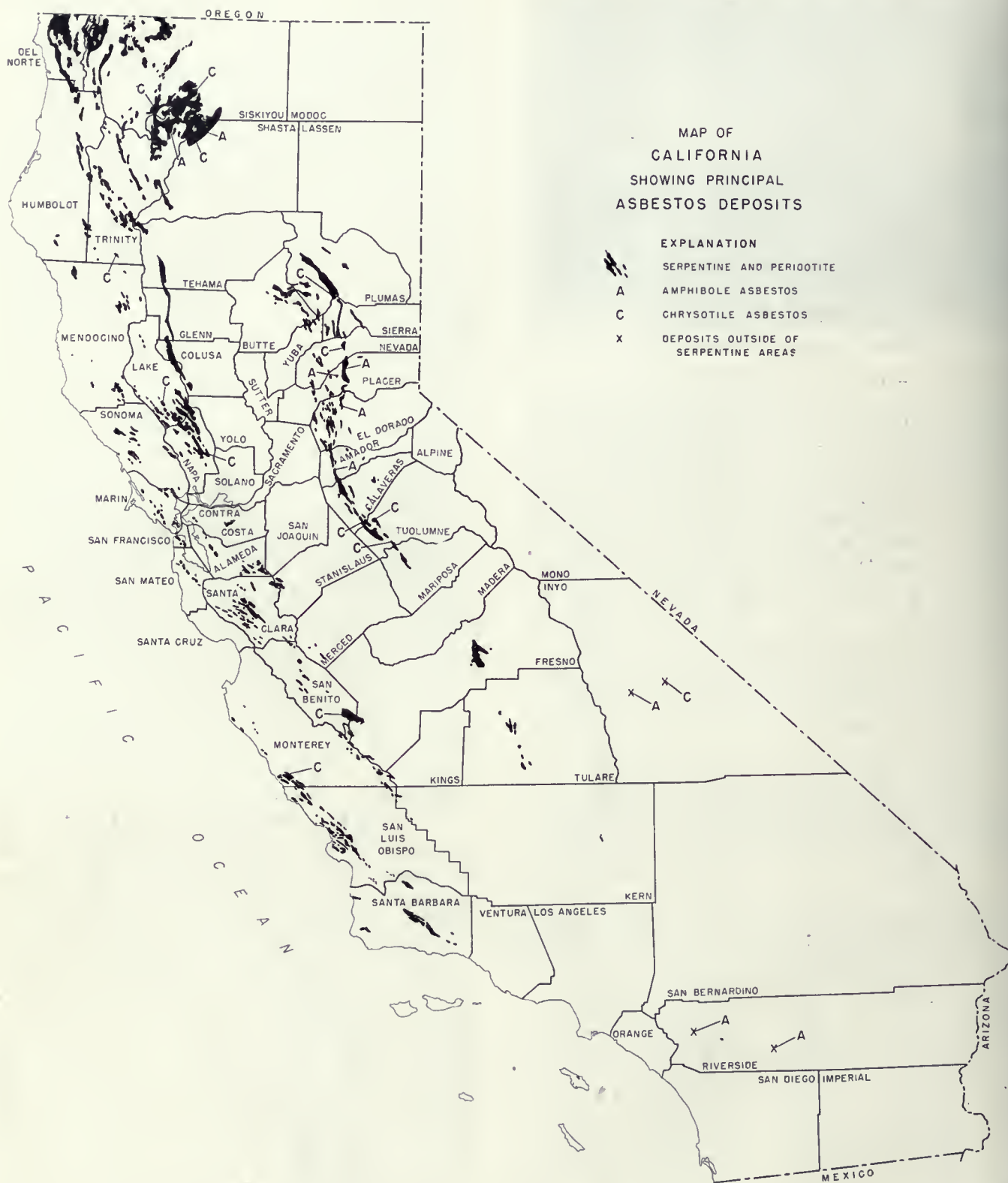


FIGURE 4.



limited to 15 counties. Table 1 shows the amount and value of all varieties of asbestos produced in California during the period 1887-1955. Most of this output has consisted of tremolite. The principal asbestos deposits of California are shown on the map, figure 4.

**Chrysotile Asbestos.** Serpentine, the host rock of chrysotile deposits, is both abundant and widely distributed in California. Figure 4 shows the distribution of massive serpentine derived from peridotite. In the southern part of the state many small bodies of serpentine have been derived by contact metamorphism of dolomite, but these are not shown on the map. Although chrysotile veins probably can be found in all of the serpentine masses in California, only about 20 deposits of potential commercial interest have been reported. Eight of these have been productive, but their outputs have ranged only from a few tons to a few hundred tons of fiber, and almost all of this was mined during the decade following World War I when asbestos prices were high.

Probably the first serious attempt to develop a chrysotile deposit in California was made at the Voorhees mine, about 7 miles southeast of Copperopolis, Calaveras County. Attempts to develop this deposit were made as early as 1904 and continued intermittently through 1927, but the total production was small. In 1954, the property was purchased by the American Asbestos Mining Corporation.

The chrysotile at the Voorhees deposit is of good quality and occurs as stockwork cross fiber veins in massive pale green serpentine. Most of the fibers are between  $\frac{1}{16}$  and  $\frac{1}{4}$  inch long, but a small percentage are up to about  $\frac{3}{4}$  inch in length. The ore body is approximately 1700 feet long and ranges from 300 to about 600 feet in width. Drill-core data have indicated that it contains an overall average of about  $3\frac{1}{4}$  percent fiber to a depth of at least 200 feet, but the fiber content is not uniform. In 1955, a composite sample of about 30 tons was systematically taken from four of the old workings and shipped to an asbestos mill for testing. It is reported to have yielded 5.24 percent fiber, about 6 percent of which was spinning fiber.\*

The Sierra chrysotile deposit near Washington, Nevada County, was worked briefly following World War I (MacBoyle, 1919), and yielded a few hundred tons of fiber. This deposit consists of stockwork veins of cross fiber chrysotile in dark green serpentine. Most of the veins are  $\frac{1}{8}$  to  $\frac{1}{4}$  inch wide, but a small percentage range up to an inch in width. The asbestos-bearing zone, which lies near the western margin of a wide north-trending serpentine mass, is approximately 1000 feet long and up to about 300 feet wide, and is exposed over a vertical range of about 500 feet on the canyon wall. Its fiber content ranges from less than 2 percent to about 6 percent, and it contains masses of barren serpentine. Mining operations began at this deposit in 1918, but were terminated in 1921 because of litigation. By 1952, the title to the property had been cleared, and in that year the deposit was explored by means of a core drilling program partially financed by a Government D.M.E.A. loan.

Several promising chrysotile prospects have been found in the large irregular serpentine mass at the junction of Trinity, Shasta, and Siskiyou Counties (Brown, 1916), but production from this area has been insignificant. Near Weed, Siskiyou County, the Shasta View prospect yielded a small amount of asbestos in 1921, but has since been idle (Averill, 1935, p. 265). At the Ratero prospect, on the north flank of Mt. Eddy, recent trenching has disclosed a rich narrow zone of ribbon fiber chrysotile veins. A relatively high percentage of the veins are between  $\frac{1}{4}$  and 1 inch in width, but the fiber is slightly harsh and most veins contain one or more central partings which reduce the apparent fiber length. Work done by 1955 had not been sufficient to indicate an ore body of commercial size.

In Shasta County the Asbestos Empress prospect, near Highland Lakes, consists of stockwork veins of cross fiber chrysotile in massive serpentine. A relatively high percentage of the veins are  $\frac{1}{4}$  to  $\frac{3}{4}$  inch wide, and some are more than  $\frac{1}{2}$  inch. The fiber is rather harsh, but strong. This deposit has been prospected by trenches, and in 1950 was core-drilled by Johns-Manville Company, but no production activity has resulted from this exploration.

Several chrysotile prospects have been found in Lake County, the most noteworthy being the Copsey and Jones prospect near Howard Springs (Brice and Goodwin, 1953). In 1928, Johns Manville Co. prospected the sheared serpentine at this locality and produced several tons of asbestos by hand cobbing cross fiber vein material from the wallrock. The chrysotile is of excellent quality and a relatively high percentage of the fiber is more than  $\frac{1}{4}$  inch long (fig. 5). However, the work done in 1928 did not reveal an ore body of commercial size and the deposit has been idle since that time.

A chrysotile deposit in Steel Canyon, near Monticello, Napa County, was mined during World War II (Davis, 1948). Most of the cross fiber chrysotile veins at this locality are less than  $\frac{1}{8}$  inch wide, and occur in sheared

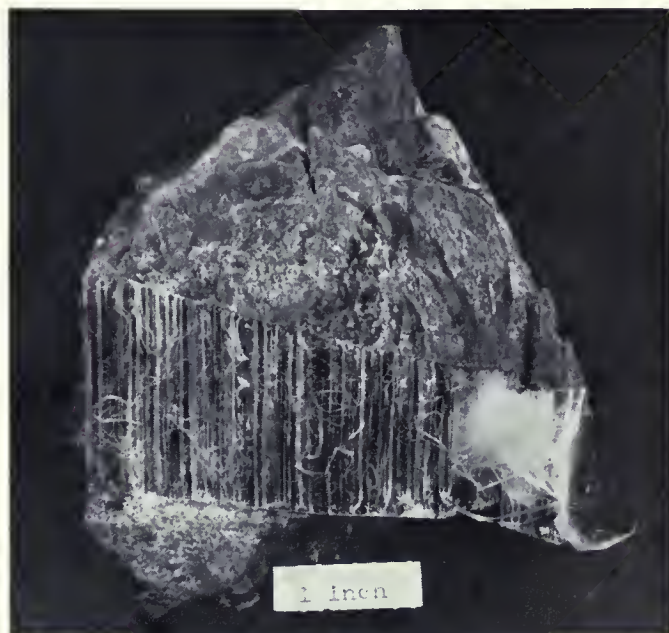


FIGURE 5. Long-fiber chrysotile from Lake County, California.

\* Drill core and sampling data kindly furnished by Mr. Lewis Cowan Merrill, American Asbestos Mining Corp.



serpentine. The rock was milled to produce a single short-fiber product, which was marketed for use in plaster and stucco for fireproofing war-plant buildings.

A small chrysotile deposit near Hernandez, San Benito County, was mined during 1925-26 (Laizure, 1926). The ore body, which consisted of stockwork veins of cross fiber asbestos near the western margin of a large mass of serpentine, was largely worked out by open cut.

A chrysotile deposit was recently found in a narrow zone of serpentized dolomite near Goldbelt Springs in the Panamint Mountains, Inyo County. The dolomite was altered adjacent to its contact with an intrusive mass of quartz monzonite, and the serpentized zone is 1 to about 4 feet wide. Chrysotile occurs as cross fiber veins which are approximately parallel the intrusive contact. In most places many closely spaced veins occupy a fiber zone which is 5 to about 20 inches wide. The fiber ranges from 1/16 to about 2 inches in length, and approximately 25 percent is longer than  $\frac{1}{4}$  inch. This prospect has been partially explored with the aid of a D.M.E.A. loan.

Other chrysotile deposits of potential commercial interest are located near Rawhide, Tuolumne County; on the Travis Ranch, southern Trinity County; and west of Bryson, Monterey County. All of these deposits are concentrations of cross fiber chrysotile veins in serpentized peridotite, and all have been partially explored in recent years.

*Amphibole Asbestos.* Tremolite is the principal type of amphibole asbestos mined in California. Small amounts of anthophyllite also have been produced, and actinolite probably has accounted for some of the output.

Commercial deposits of tremolite are small, ordinarily consisting of single, narrow, slip fiber veins in serpentine or other metamorphic rocks. The quality of the fiber characteristically varies from place to place in the vein. Only a small percentage of the asbestos is marketable, and this must be hand-picked. As a result of the limited market for tremolite and the expense of handling much waste rock, these veins are seldom mined to depths of more than about 25 feet.

Tremolite asbestos has been found in most of the counties of the Sierra Nevada and Klamath Mountains, where it occurs as slip fiber veins in fault zones in serpentine. Such veins are ordinarily no more than a few inches wide, but some of them contain lenticular pockets of fiber several feet wide. For example, a vein at the Sylvester mine in Shasta County ranges in width from a few inches to about 30 inches over the 110 feet that it has been followed in mining. The best quality asbestos, which lies in the center of the vein, is white and finely fibrous, but has a very low tensile strength. A maximum of 6 inches of hard greenish asbestos, called bone rock, occurs on each wall of the vein (O'Brien, 1948). This mine has yielded about 60 tons of tremolite asbestos. A tremolite deposit at the nearby Loma Blanca mine is a lens 15 feet or more wide and at least 50 feet long. Both of these veins are enclosed in serpentine.

Small production has been obtained from several tremolite asbestos veins in Placer County, principally in the vicinity of Iowa Hill. Most of the veins are at the contact between serpentine and metasedimentary rocks, and range from a few inches to several feet in width. The white slip fiber is ordinarily hard and somewhat brittle

when mined, but when allowed to weather at the surface for a year or two it becomes silky and flexible. The weathered fibers are of excellent quality and are about a foot in maximum length. This asbestos has been marketed principally for use as acid filters.

Near Keeler, Inyo County, slip fiber tremolite of excellent quality has been produced from a fault zone that traverses limestone and dolomite. Much of the fiber in this vein is intergrown with calcite, and is not of commercial value.

At Pinyon Flat, Riverside County, a fault zone in hornblende schist contains slip fiber tremolite in veins up to about 2 feet wide. About a thousand tons of fiber is reported to have been produced from Pinyon Flat, principally for use in the manufacture of battery boxes (Tucker and Sampson, 1945).

An unusual type of anthophyllite asbestos, with fibers about as strong as those of chrysotile, has been mined at two localities in California. At one of these localities, near the mouth of Coffee Creek in Trinity County, soda-rich anthophyllite occurs as cross fiber veins in serpentine and is similar both in appearance and tensile strength to chrysotile. The fibers are as much as 2 inches in length (Laudermilk and Woodford, 1930). About 10 tons of crude fiber, vein material hand cobbled free of wall rock, was produced from this deposit in 1930 (Averill, 1931). At the Morgan mine, near Towle, Placer County, a narrow slip fiber vein of soda-rich anthophyllite occurs in a fault zone in serpentine. The fiber is gray-green and has a high tensile strength. About 5 tons of this fiber was mined during World War I, but the property has been idle since then. No deposits of the more typical mass fiber anthophyllite have been reported in California.

Crocidolite occurs at a number of places in the Coast Ranges as veinlets and bunches in iron-rich metachert, but no deposits have been found that contain fibers sufficiently flexible to be of value as asbestos. Amosite is not known to occur in California.

#### MINING METHODS, TREATMENT, AND GRADING

Because asbestos deposits differ widely in character from place to place, a great variety of methods has been used in mining them. Most of the chrysotile deposits that occur in massive serpentine must be mined cheaply because of the low grade of such deposits and the high milling costs. Thus in the initial stages of mining such deposits, open-pit methods are employed where possible, and are followed if necessary and practical by large-scale underground methods such as block caving (Briggs, 1955). Glory-hole, room-and-pillar, shrinkage-stopping, and other methods also have been used to suit local conditions.

Amphibole asbestos, which occurs mostly in narrow seams and small pockets, must generally be mined by trenching or in drifts and tunnels which follow erratic ore-bodies. As this type of operation is relatively expensive, only the best quality fiber can be mined if any profit is to be made. Mass fiber anthophyllite is mined by open pit.

Chrysotile offers difficult milling problems because of the fibrous and flexible character of the mineral and low grade of the mined rock (Sinclair, 1952). Ordinary treatment methods are not applicable because the fiber



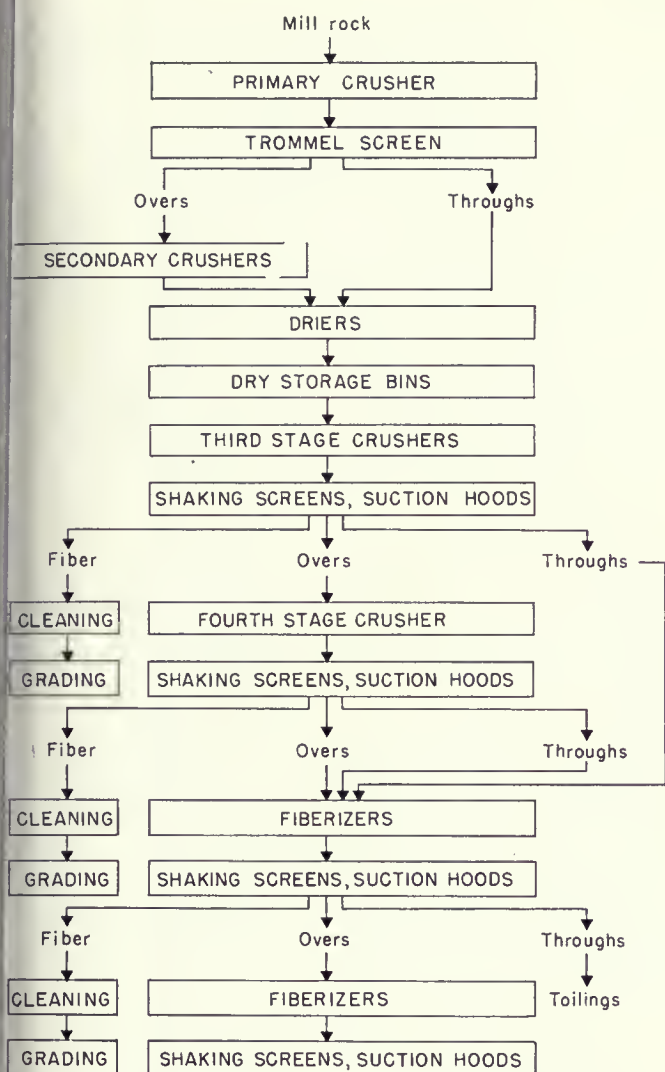


FIGURE 6. Typical flow sheet of a Canadian asbestos mill.  
(After Bowles, 1955.)

has essentially the same specific gravity and chemical composition as the host rock. In addition, not only must the fiber recovery be as large as possible, but the more valuable long fibers must not be broken or damaged in the process. Milling generally consists of repetitive crushing and screening, and removal of the fiber after each stage, as soon as it is released from the rock, with air suction hoods.

A typical mill flow sheet (fig. 6) would include primary and secondary rock crushing to 3-inch size, furnace drying to remove moisture, and third-stage crushing to free the fiber. The third-stage crushing product, about  $\frac{1}{2}$ -inch size, flows to a shaking screen. Gravity concentration occurs as the material moves along the screen, producing a layer of light-weight fiber on top of a layer of heavier rock, and the fines and dust drop through the screen. The light-weight fiber is removed through a suction hood installed at the end of the screen. The oversize rock flows over the end of the screen and is crushed to  $\frac{1}{4}$ -inch size and rescreened as outlined above. The undersize is fed to a fiberizer, consisting of high-

speed hammers which break the rock by impact, making a further separation of rock and short fibers. The latter are separated by another suction-screening operation. When free, the fiber is passed to a two-level screen for size classification. The shorts drop through both screens, the medium-length fiber is removed by air suction from the end of the lower screen, and the long fiber is similarly removed at the end of the top screen (Bowles, 1955).

Since 1950, a new type air-swept ball mill, designed to process the ore in a single stage, has been installed in several chrysotile-treatment plants in Canada (Mining World, 1955; Beals, 1955).

Crocidolite and amosite asbestos more than half an inch long are recovered largely by hand cobbing. However, at some African deposits the ore with shorter fiber is milled in a manner similar to that used for chrysotile.

Mass fiber anthophyllite is simply crushed and fiberized. Tremolite is ordinarily hand sorted at the mine and shipped without treatment.

Industry-wide standards for grading asbestos have been established only for chrysotile. Consequently, the quoted prices for the following grade specifications apply only to chrysotile asbestos. To determine with reasonable accuracy the quality of fibre in each grade and thus be able to modify grading methods accordingly, a standard testing machine is used. The machine consists of a nest of four wooden boxes, measuring  $24\frac{1}{2}$  inches in length,  $14\frac{3}{4}$  inches in width, and  $3\frac{1}{2}$  inches in depth. The boxes, which are superimposed one above the other, are numbered from the top down 1, 2, 3, and 4. The bottoms of boxes numbers 1, 2, and 3 are made of metallic screen of the following specifications: box no. 1,  $\frac{1}{2}$  inch opening; box no. 2, 4 mesh; box no. 3, 10 mesh. Box no. 4 is a receptacle for the fines which fall through the three other boxes. The nest of four boxes or trays rests on a vibrating table to which an eccentric having a throw of  $\frac{2\frac{5}{8}}{1\frac{7}{8}}$  inch gives a movement of  $1\frac{7}{8}$  inches.

To make a test, 16 ounces of chrysotile asbestos is put on the covered top tray. The machine is run at the rate of 300 r.p.m. at the shaft of the eccentric for a period of 2 minutes, giving the nest a horizontal shaking motion. At the end of this time, the asbestos which remains on each tray is weighed. This gives the grades of the asbestos fiber; the longest fiber stays on the top tray whereas the shorter fiber, according to its length, remains on screens 2 and 3 or drops into the pan or lowest tray. The more retained on the first screen and the less fiber in the pan, the higher the grade and therefore the greater its value. If, for example, a customer buys spinning fiber of the specification 4-7-4-1, it means that in a sample of 16 ounces, 4 ounces will remain on the top screen, 7 ounces on the second, 4 on the third, and 1 ounce will pass through all screens to the pan. Material of this grade will sell for more than a poorer grade, such as paper stock testing 0-0-10-6. This designation indicates that in a pound of asbestos tested, none is retained on the first and second screens, 10 ounces remain on the third, and 6 go through to the pan.

Chrysotile is marketed as either crude or milled fiber. Crude fiber, which commands a higher price than the milled product, is defined as hand-cobbed vein material essentially in its native or unfiberized form. Except for the very lowest grades, which are based on weight per cubic foot, all milled grades are based on the results of



tests in the standard testing machine previously described. The following is a description of the standard grades of chrysotile asbestos (Ross, 1931, p. 48).

Class	Standard designation of grade	Description
Group #1	Crude #1 -----	Basically crude $\frac{3}{4}$ inch staple or longer
Group #2	Crude #2 -----	Basically crude $\frac{3}{8}$ inch staple up to $\frac{3}{4}$ inch
Milled Asbestos		
Group #3	Spinning fiber----	Fiber testing 0-8-6-2 and over
Group #4	Shingle fiber----	Fiber testing below 0-8-6-2 to and including 0-1 $\frac{1}{2}$ -9 $\frac{1}{2}$ -5
Group #5	Paper fiber -----	Fiber testing below 0-1 $\frac{1}{2}$ -9 $\frac{1}{2}$ -5 to and including 0-0-S-8
Group #6	Waste, stucco or plaster-----	Material testing below 0-0-S-8 to and including 0-0-5-11
Group #7	Shorts or refuse--	Material testing 0-0-5-11 and below, including material testing 0-0-1-15 and weighing 35 pounds or less per cubic foot, loose measure

#### UTILIZATION

Most of the important uses of asbestos are based upon the fact that it has physical characteristics similar to those of organic fibers, yet it is both noncombustible and noncorrosive. If sufficiently long to be spun, fibers of chrysotile and crocidolite are woven into fabrics that find a wide variety of applications. The largest use of asbestos textiles is in the manufacture of friction materials such as automobile clutch facings and brake linings. Asbestos fabrics are also used for manufacturing such items as fireproof clothing, theater curtains, lagging cloth, electrical insulation products, and conveyor belts for carrying hot materials. Asbestos cloth treated with rubber is made into special air- and liquid-tight gaskets.

The nonspinning grades of asbestos are used in the manufacture of numerous products in which the asbestos acts as a reinforcing agent or as a friction or insulation material. One of the most important uses of short fiber chrysotile and crocidolite is in the production of asbestos-cement construction materials. These products are composed principally of portland cement and contain up to 30 percent asbestos as a reinforcing agent. They include pipe, shingles, wallboard, corrugated sheets, and many other structural forms. The uses of asbestos-cement products have increased rapidly in recent years. This is particularly true of asbestos-cement pipe, now widely used for sewer, water, and gas mains, because it resists corrosion, is nonconductive and relatively shockproof, and compares favorably in strength with cast iron (Bowles, 1955, p. 13). One of the best known heat insulation materials is composed of 85 percent basic magnesium carbonate and 15 percent asbestos.

The shorter grades of chrysotile are mixed with a small amount of binder and compressed into asbestos paper and millboard, which also are important heat-insulation materials. Much short fiber chrysotile is used in the manufacture of molded brake bands and clutch facings, which consist essentially of asbestos fibers bonded with an organic matrix and reinforced with wire. These are rapidly replacing the woven facings. In

recent years there has been increasing use of the very short grades of chrysotile, especially in the manufacture of asphalt and plastic floor tiles, which may contain 35 percent or more of asbestos.

The uses of tremolite and anthophyllite asbestos are limited because of low fiber strength. They are used principally as fillers in asphaltic, plastic, and rubber products and for welding rod coatings. These varieties, along with crocidolite, are also used for chemical filters. The amphibole varieties are all acid resistant whereas chrysotile is relatively soluble in acids. Short fiber tremolite and chrysotile are used in fire-resistant paints.

Amosite is of considerable value as felted lagging for high temperature insulation and as felted, loosely compacted covering for marine turbines, jet engines, and for similar applications. It is also used with chrysotile in 85 percent magnesia block and pipe covering insulation.

In 1954, the apparent total consumption of asbestos in the United States was 724,117 short tons, valued at \$60,263,411. Of this, 47,621 short tons valued at \$4,697,962 were produced from mines within the United States, principally in Vermont and Arizona. Most of the remainder was imported from Canada (U. S. Bureau of Mines, Mineral Market Report MMS No. 2480, Feb., 1956).

The total value of asbestos products manufactured in the United States during 1954 was about \$405,000,000 as compared with a total value of about \$267,000,000 in 1947. The approximate proportional values of the different types of asbestos products manufactured during 1954 were as follows: asbestos cement products, 32 percent; floor tiles, 23 percent; friction materials, 19 percent; insulation materials, 12 percent; gaskets, 5 percent; textiles, 4 percent; packing, 4 percent; unspecified, 1 percent.

#### MARKETING PROBLEMS IN CALIFORNIA

Prior to the recent industrial boom, the market for asbestos on the West Coast was relatively limited. Most of the plants for manufacturing asbestos products were, and still are, located in the industrial areas in the eastern part of the United States. However, since World War II several new fabrication plants have been constructed in California and older ones have been enlarged so that asbestos consumption is steadily rising in this area. Most of the new plants are branches of large eastern firms.

The principal asbestos products manufactured in California are asbestos-cement construction materials, insulation materials, and composition flooring and roofing. Chrysotile is almost exclusively the variety of asbestos utilized, although a minor amount of crocidolite is used in asbestos-cement products and anthophyllite is used as a filler in some flooring products. Recent consumption of chrysotile in California has been estimated at between 75,000 and 100,000 tons per year, almost all of which is imported from Quebec.

Most of the large producers of raw chrysotile in Canada also manufacture finished asbestos products at plants in the United States. These firms usually are not interested in purchasing raw fiber, but many of them have expressed considerable interest in obtaining deposits in California.



## PROPERTIES OF ASBESTOS FIBERS

Modified after Bodollet (1951)

	CHRYSOTILE	TREMOLITE	ACTINOLITE	CROCIDOLITE	AMOSITE	ANTHOPHYLLITE
COLOR	Green, greenish-yellow, gray, or white	White, grayish-white, greenish-yellow, or bluish gray	Green	Lavender, blue, or greenish	Ash-gray, greenish, or brown	Grayish-white, brownish-gray, or green
TEXTURE	Soft to harsh, silky	Generally harsh, some soft	Harsh	Soft to harsh	Coarse, but somewhat pliable	Harsh
MINERAL ASSOCIATION	In serpentine	In serpentine, Mg limestones and various metamorphic rock	In serpentine and crystalline schists	Iron-rich siliceous argillite in quartzose schists	In crystalline schists, etc.	In crystalline schists, gneisses or meta-serpentine
VEINING	Cross & slip fibers	Slip or moss fiber, rarely cross fiber	Slip or moss fiber	Cross fiber	Cross fiber	Moss or slip fiber, rarely cross fiber
LENGTH	Short to long	Short to long	Short to long	Short to long	Mostly long	Short
TENSILE STRENGTH lb/sq. in.	80,000 to 100,000	8,000 or less	1,000 or less	100,000 to 300,000	16,000 to 90,000	4,000 or less
FLEXIBILITY	Very flexible	Fairly flexible to brittle	Brittle to slightly flexible	Flexible	Flexible	Mostly brittle
SPINNABILITY	Very good	Generally poor, rarely spinnable	Poor	Fair	Fair	Very poor
FUSIBILITY	Fusible at 6	Fusible at 4	Fusible at 4	Fusible at 3	Fusible at 6	Infusible or difficultly fusible
ACID RESISTANCE	Poor	Good	Fair	Good	Good	Very good

FIGURE 7.

Independent manufacturers of asbestos products must depend upon surplus production from captive mines of other firms or upon the relatively few non-captive mines for a source of raw asbestos. Many of these independent manufacturers are located in California, and the large freight rate from Quebec should enable any well-organized chrysotile mining operation in the state to obtain local markets. In January, 1957, the freight rates on raw asbestos fiber from the mines in Quebec to either Los Angeles or San Francisco ranged between \$32.80 and \$37.20 per ton in 40-ton carload lots. Nevertheless, the miner attempting to establish markets for fiber from a California chrysotile deposit is faced with many obstacles. Most important of these is the necessity of being able to guarantee a continuous supply of asbestos meeting certain specifications. Large-scale fabricators of asbestos products are reluctant to change from a known source of supply to one of uncertain quality and longevity. Thus the miner must initially invest large sums of

money in exploration and mill construction in order to supply bulk samples of the fiber for examination and testing.

Late in 1956 the price quotations for the various grades of chrysotile produced in Quebec, per ton f.o.b. mine, were as follows:

Group #1 (Crude #1)	-----	\$1,400 to \$1,725
Group #2 (Crude #2)	-----	750 to 1,100
Group #3 (Spinning fiber)	-----	350 to 575
Group #4 (Shingle fiber)	-----	170 to 225
Group #5 (Paper fiber)	-----	110 to 140
Group #6 (Waste, stucco, or plaster)	-----	82
Group #7 (Shorts or refuse)	-----	38 to 75

The market for tremolite asbestos is very small, and generally only the best quality hand-picked fiber is marketable. As there are no standard specifications or quotations for tremolite, the price is determined entirely by negotiation between miner and purchaser. Since 1950, tremolite sales have been reported ranging from \$50 per



ton to about \$600 per ton, depending upon quality and ultimate use of the fiber. Firms purchasing a ton or two of tremolite for highly specialized uses are often willing to pay a much higher price for good fiber than large-scale users who can more easily obtain fiber of good quality from cheap foreign sources.

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## ASPHALT AND BITUMINOUS ROCK

By CHARLES W. JENNINGS

In the early development of roads in California, local deposits of bituminous rock, particularly in Los Angeles, Santa Barbara, San Luis Obispo, Kern, Santa Cruz, and Mendocino Counties, were mined as sources of natural asphalt for surfacing material. These deposits were most productive during the years 1910 and 1911. In later years, natural asphalt from bituminous rock was largely replaced by asphalt products manufactured by petroleum refineries. These manufactured products are more uniform and of higher grade than the natural material and permit better control of physical properties. In 1947-48, only one bituminous rock quarry was operating in the state, and since 1949 no bituminous rock has been mined. During World War II and in later years, the larger deposits of bituminous rock in California were seriously studied as possible sources of material from which oil may be extracted; several of the larger bituminous rock deposits were mapped in detail by the U. S. Geological Survey; a detailed study of oil-impregnated strippable deposits was undertaken for the U. S. Corps of Engineers, Department of the Army; and several oil companies investigated the problem of recovering petroleum from such rocks. Analyses of radioactive asphalt-bearing rocks of California, made recently by the U. S. Geological Survey, show that the petroleum ash fraction of the bituminous rock contains as much as 1.9 percent uranium.

### COMPOSITION AND GEOLOGIC OCCURRENCE

Native asphalt consists of heavy liquid, semi-solid, and solid hydrocarbon residues which have been deposited in surface and near-surface rocks and soil. Such deposits occur where liquid petroleum has migrated upward and lost its lighter fractions by evaporation. This process results in various types of accumulations of bituminous material, ranging from seeps and pools of almost pure heavy petroleum to rock in which petroleum residue fills a fraction of the pore space. Such terms as "tar sand", "oil shale", and "asphalt rock" are included in the more general term "bituminous rock" which refers to any rock that carries a substantial amount of petroleum. The so-called "oil-shale" in California contains hydrocarbons in the form of natural petroleum, but elsewhere, as near Rifle, Colorado, the term "oil shale" commonly refers to rocks that contain a carbon compound, known as kerogen, which is not petroleum, but which can be processed to yield petroleum products. "Petroleum asphalt" is the term applied to the material manufactured at petroleum refineries by distillation (fig. 1). Petroleum asphalt production in the United States now far outranks bituminous rock production.

Various peculiar hydrocarbon substances which usually are considered as separate mineral species, but which are closely related to asphalt, occur at widely distributed localities in the Coast Ranges of California. Gilsonite has been noted near Sisquoc in Santa Barbara County; amber in the Simi Valley in Ventura County; curtissite in serpentine in San Francisco, and with cinnabar in Lake, Napa, and Sonoma Counties; aragotite associated with cinnabar in Napa and Santa Clara Coun-

ties; napalite in cinnabar mines in Napa County; and posepnyte in the cinnabar mines of Lake and Napa Counties. Chemically, these substances are hydrocarbons and commonly contain oxygen. They have not proved to be of commercial importance in California and of these only gilsonite is mined commercially in the United States.

Most asphaltic rock deposits occur in sandstone, limestone, and shale. In igneous rocks they are rare and small and generally are near petroliferous sedimentary source beds. In California, native asphalt occurs as seepages or as impregnations of the interstices of porous rocks; the harder asphalt and asphaltites most commonly fill fissures and resemble dikes and sills.

Asphaltic material, like petroleum from which it is derived, has the ability to migrate from the place of its origin. The main factors affecting movement of native bituminous substances are hydrostatic pressure (flotation upon ground water), gas pressure, capillary action, differential compaction, and heat.

Petroleum is probably the mother substance from which other bituminous substances are derived. The process of conversion of petroleum to asphalt is known as metamorphosis and is controlled by time, heat, and pressure.

### LOCALITIES IN CALIFORNIA

Known deposits of bituminous rocks in California are very numerous, and they generally lie within the limits of the distribution of marine Miocene and Pliocene formations in and around the margins of the Tertiary basins. Figure 2 shows the location of asphalt and bituminous rock deposits in California, and a description of these is tabulated by counties in table 1.

In 1944, 1945, and 1951, the United States Geological Survey published a series of five sheets, each containing a preliminary map and a brief text on specific bituminous rock deposits in California (Holmes, Page, and Duncan, 1951; Page, Williams, and Henriksen, 1944; Page, Henriksen, Williams, and Moran, 1945; Page, Williams, and Henriksen, 1945; and Williams and Holmes, 1945). These deal with the occurrences of bituminous rock near Santa Cruz, Santa Cruz County; Casimolia, Santa Barbara County; Edna, San Luis Obispo County; McKittrick, Kern County; and Point Arena, Mendocino County. The following paragraphs summarize these investigations and also include brief descriptions of the bituminous sands east of Newhall, and the famous tar pits of Rancho La Brea in west Los Angeles.

*Santa Cruz, Santa Cruz County.* Bituminous rocks are discontinuously exposed in two areas, each about one mile square, 4 to 6 miles northwest of Santa Cruz. These have been identified as the Calrock quarry area and the Cowell and City Street Improvement Company areas on the index map shown in figure 3. Cenozoic sedimentary rocks exposed in the region dip 3° to 7°, and overlie pre-Cretaceous quartz diorite basement rocks. The bituminous deposits are interbedded in sandstone or occur as sandstone intrusions.



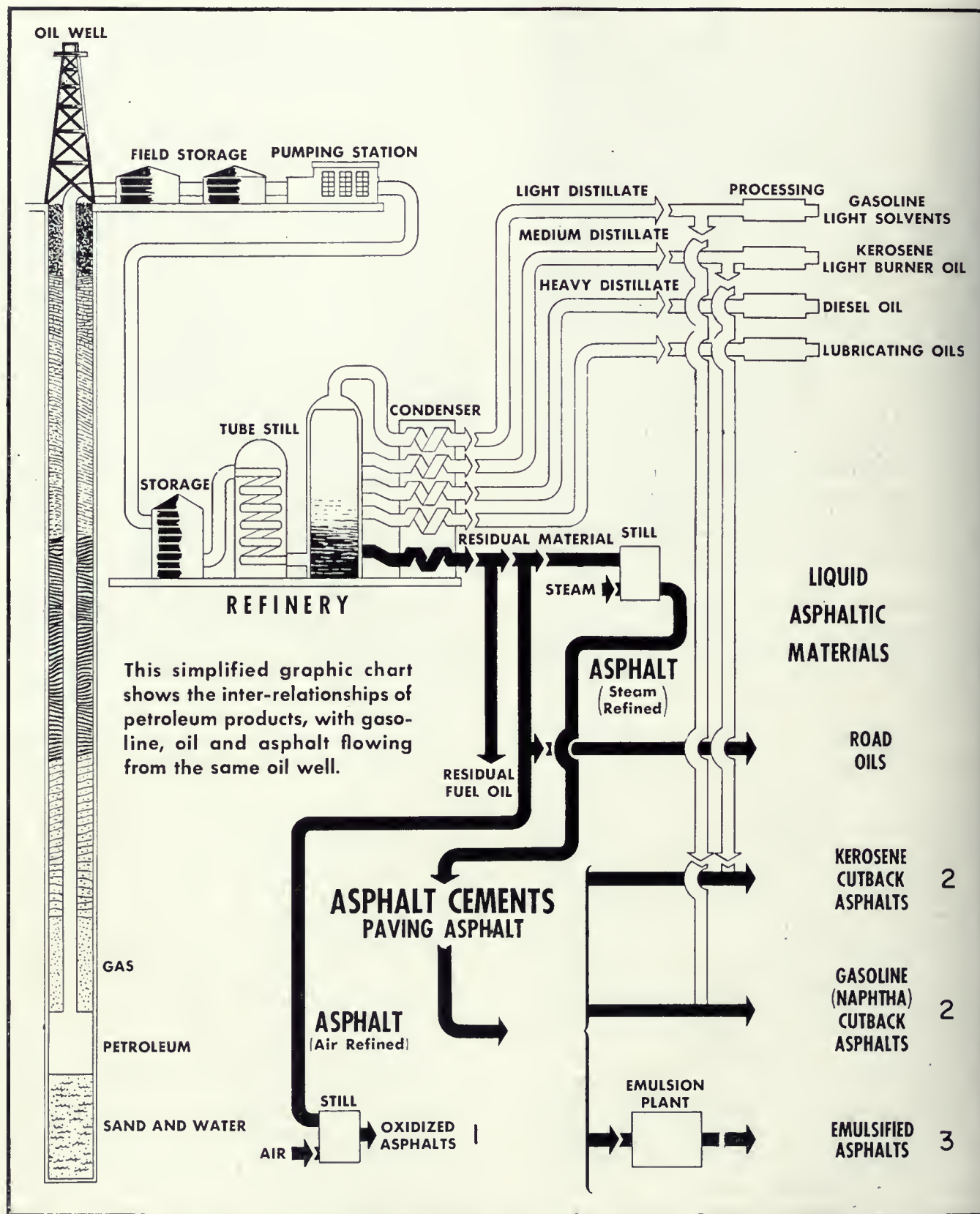


FIGURE 1. Petroleum asphalt flow chart. (1) *Oxidized asphalt*: a higher melting-point asphalt produced by blowing air through heated asphalt. (2) *Cutback asphalt*: asphalt liquefied with a volatile petroleum distillate; the distillate evaporates on exposure to air, leaving asphalt cement. (3) *Emulsified asphalt*: an emulsion of asphalt and water with an emulsifying agent. Courtesy of the Asphalt Institute.



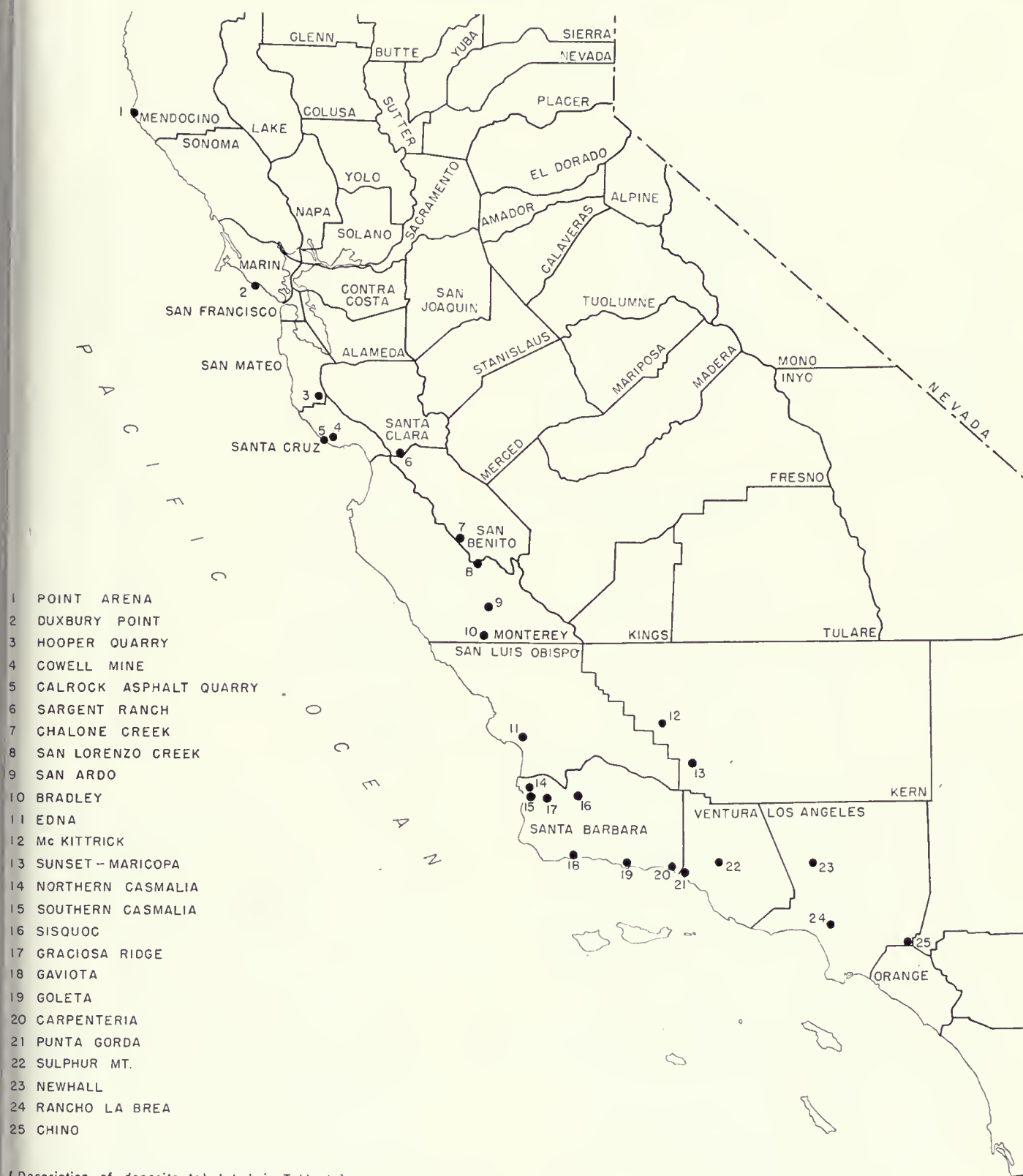


FIGURE 2. Location of the more noteworthy asphalt and bituminous rock deposits in California.



Table 1. Asphalt and bituminous rock deposits of California.

Map No.	County	T-R-S	Name of deposit or locality	Age and formation	Overburden	Type of deposit, thickness of beds, and dip	Bitumen content and reserves	Production history, references, and remarks
1	Mendocino	T12N-R17W	Point Arena (2 areas: Arena Cove and Porter O'Neal ranch)	Miocene Monterey		Bituminous sandstone. 4 beds: 1'-30' thick, 18° to 55° dip.	6½% bitumen by weight, or 15.6 gals/ton. Indicated and inferred reserves = 3,232,000 tons containing 1,207,000 bbls. bitumen.	Some early production. Holmes 1951, OM 125.
2	Marin		Duxbury Point, North (2 miles NW of Bolinas) along sea cliffs.	Miocene Monterey		Asphalt dike, residues from oil seepages. Steep dip.	Minor	No production. Calif. Div. Mines B 118, p. 621.
3	San Mateo	T8S-R3W-S8	Hooper quarry (abandoned).			Bituminous rock.		Some used for private roadwork. 17th Rept. State Mineralogist, p. 169.
4	Santa Cruz	T11S-R2W-S5	City Streets Improvement Co., Cowell Mico.	Miocene Monterey	Few feet to 100'	Bituminous sandstone and fissure fillings. 1' to 30' thick. 3° to 7° dip.	Ave. bitumen content = 12%. Reserves in Santa Cruz area = 9,300,000 cu. yds. or 10,000,000 bbls. asphalt.	Worked extensively for paving rock between 1888 and 1930. Page, 1945, Map 27.
5	Santa Cruz	T11S-R3W-S12	Calrock Asphalt Co.	Miocene Monterey and Vaqueros, and on pre-Cretaceous quartz diorite.	Few feet to 100'	Bituminous sandstone and fissure fillings. 1' to 35' thick. 3° to 7° dip.	Ave. bitumen content = 10%. Reserves in Santa Cruz area = 9,300,000 cu. yds. or 10,000,000 bbls. asphalt.	Worked from 1930 to about 1949 for paving rock and pressed asphalt bricks for flooring. Oil extraction experimental project begun in 1955. Page, 1945, Map 27.
6	Santa Clara		Sargent Ranch (vicinity of Sargent oil field).	Miocene Monterey and Pliocene Purisima.		Extensive oil and tar seeps and bituminous sandstone.		Some early production from tunnel. Davis & Jennings, 1954, p. 383-385.
7	San Benito	T17S-R5E-S32 & 33	Chalone Creek (Matthews quarry, east of Metz).	Miocene Monterey adjacent to granite.		Asphalt-impregnated arkose.		Some early production. Eldridge, 1900, p. 407-409.
8	Monterey	T19S-R9E-S15	San Lorenzo Creek, Mylar quarry (10 mi. NE of King City).	Miocene Monterey.		Asphalt impregnated arkose and bituminous sandstone 1500' long, 100' wide.		Some early production for road paving. Eldridge, 1900, p. 407-409.
9	Monterey	T22S-R10E-S18, 19, 29, 32, 33	San Ardo (West side Salinas River).	Miocene Monterey.	Thick	Bituminous sandstone 125' thick, 4 mi. long. Steep dip.	Bitumen content generally small.	Eldridge, 1900, p. 410-411.
10	Monterey	T24S-R10E	Bradley (6 mi. SW Bradley along San Antonio R.).	Miocene Monterey and Pliocene Pleistocene Paso Robles.		Bituminous sandstone 30' thick, 3000' long. 40°-85° dip.		Eldridge, 1900, p. 411-412.
11	San Luis Obispo	T31S-R12 & 13E	Edna district.	Mio-Pliocene Pismo.	Little or no overburden.	Bituminous sandstone. Gentle dip.	26 gal. oil per ton. 11% bitumen by weight. Reserves = 282,880,000 tons.	Past production from 27 quarries for paving. Oil extraction experiment during World War II. Page, 1944, Map 16, Shea & Higgins, 1945.
12	Kern	T30S-R22E-S19, 20, 21, 28, 29	McKittrick (Asphalt) district.	Mostly in Pliocene Pleistocene Tulare. Some in Pliocene Etchegoin and Miocene Monterey.	Thick	Scattered asphalt and bituminous sandstone.	24 gal. oil per ton. Reserves = 8,500,000 to 15,700,000 tons. Recoverable bitumen = 4,850,000 to 9,000,000 bbls.	Extensive mining in past. Page, 1945, Map 35.
13	Kern	T11N-R23W-S18, 19, 20. T11N-R24W-S13, 14	Sunset-Maricopa district.	Miocene		Asphalt and tar sands 2'-15' thick.		18th Rept. State Mineralogist, 1922, p. 230.
14	Santa Barbara	T9N-R35W-S3, 10	Northern Casmalia area (N.T.U. mine).	Mio-Pliocene Sisquoc		Asphaltic diatomite including dikes and veins. 20°-40° dip.	42 gal. oil per ton. Quarry contains 100,000 tons reserves.	Extensively mined first as fuel then for paving. Williams & Holmes, 1945, Map 34.
15	Santa Barbara	T9N-R35W	Southern Casmalia (Airox mine near Schumann).	Mio-Pliocene Sisquoc	40' (?)	Oil impregnated diatomite including dikes and veins. Averages 300' thick. 20°-40° dip.	75,000,000 tons inferred reserves.	Extensively mined and burned for lightweight aggregate.
16	Santa Barbara		Sisquoc region (Alcastraz mine, Zaca Creek area, area east of Los Alamos).	Pliocene Careaga	15' average	Bituminous sandstone 185' maximum thickness, 85' average thickness.	30 gal. oil per ton. 41,000,000 tons primary reserves.	Oil extracted by solvents during 1900 and piped 35 miles to refinery on coast. Eldridge, 1900, p. 429-438, 15th Rept. State Mineralogist, 1915, p. 734.



Table 1. Asphalt and bituminous rock deposits of California.—Continued.

Map No.	County	T-R-S	Name of deposit or locality	Age and formation	Overburden	Type of deposit, thickness of beds, and dip	Bitumen content and reserves	Production history, references, and remarks
17	Santa Barbara		Graciosa Ridge in Santa Maria (Orcutt) oil field.	Pliocene Careaga	Considerable	Bituminous sandstone including asphalt veins. 20' to 70' thick. Steep dip.		Mined by shaft and tunnel. Eldridge, 1900, p. 426-429, 15th Rept. State Mineralogist, 1915, p. 733.
18	Santa Barbara		Gaviota coastal area.	Mio-Pliocene Sisquoc and Miocene Monterey.		Bituminous sandstone. 25' thick maximum. High dip.	16-19 gals. per ton.	No production. Eldridge, 1900, p. 440-441.
19	Santa Barbara		Goleta area (La Patera mine, More's Landing).			Irregular pockets and veins each having 750-1500 tons bituminous material. Steep dip.	High grade material resembling gilsonite.	Formerly mined underground. Eldridge, 1900, p. 441-443, 15th Rept. State Mineralogist, 1915, p. 734.
20	Santa Barbara		Carpenteria area (along beach).	Miocene Monterey	12'-50'	Bituminous sandstone. 12'-30' thick. Flat lying.	18%-20% bitumen content.	Worked extensively by several quarries for paving. Eldridge, 1900, p. 444-445, 15th Rept. State Mineralogist 1915, p. 731-732.
21	Ventura	T4N-R25W-S1	Punta Gorda area.	Miocene Monterey (?)		Bituminous sandstone. 4' thick. Steep dip.	28% asphaltum	Mined in 1895 by shaft and tunnel. Eldridge, 1900, p. 445-446, 15th Rept. State Mineralogist, 1915, p. 754.
22	Ventura	T4N-R22W S3 & 10	Sulphur Mt. (Ojai Mine).	Miocene Monterey		Seepages of heavy viscous bitumen over rather large area.		15th Rept. State Mineralogist, 1915, p. 754.
23	Los Angeles	T4N-R15W-S7 T3N-R15W-S18 & 19	Newhall area (includes Elsmere Canyon, Whitney Canyon, and Placerita oil fields).	Chiefly in Pliocene Repetto and Pico. Also in pre-Cretaceous gneiss and schist, Eocene, and Pleistocene beds.		Bituminous sandstone and tar seeps.		Oakeshott, G. B. (in press) Bull. 172.
24	Los Angeles		Rancho La Brea (near old Salt Lake oil field).	U. Pleistocene terrace deposits.		Tar pits and asphalt.		Stock, 1949.
25	Los Angeles		Chino area (4 mi. SW of Chino).			Bituminous sandstone. 20' maximum thickness, 6'-12' average thickness. 15° dip.		Eldridge, 1900, p. 447-448.

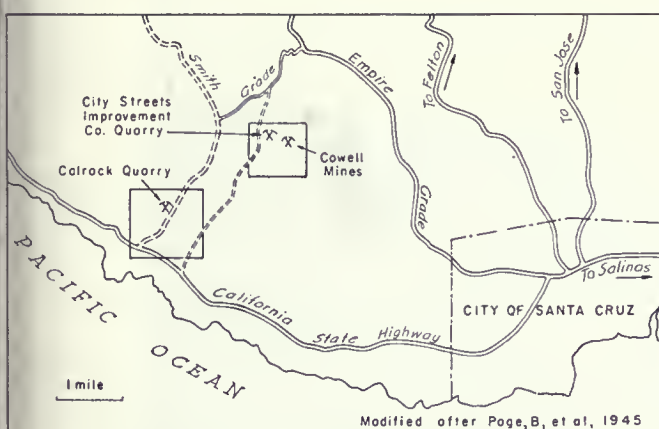


FIGURE 3. Index map of Santa Cruz region showing areas of bituminous rock quarries.

Most of the deposits in the Calrock quarry area occur immediately above the quartz diorite, or above the lower Miocene Vaqueros sandstone. The bituminous beds may be a part of the Vaqueros formation. These deposits range in thickness from 1 to 35 feet. In addition, many small bituminous dikes project into shale of the middle

Miocene Monterey formation, and large sill-like bodies have been mined. In the Cowell mine area, the bituminous sandstone deposits occur as interbedded shale and sandstone strata of the Monterey formation and as sills. The thickest deposits are 8 to 30 feet thick in this area and are essentially flat-lying. The U. S. Geological Survey estimates reserves of bituminous rock in the two areas total 9,300,000 cubic yards, or about 10,000,000 barrels of asphalt (Page, 1945). The bitumen<sup>1</sup> content of the sandstone is ordinarily between 10 and 18 percent by weight.

Between 1888 and 1915 the deposits in both areas were worked by several companies, including the City Street Improvement Company and the Cowell Company. During this period approximately 614,000 tons of bituminous rock, valued at about \$2,352,300, were produced and sold for paving, but the output dwindled gradually in succeeding years, and by 1930 most of the workings were idle. In that year Calrock Asphalt Company began using the material for paving and for making pressed asphalt bricks for industrial flooring. About 1949, these operations ceased and no production of bituminous rock has been recorded from the Santa Cruz area since then.

<sup>1</sup> In an asphaltic product, bitumen is that portion which is completely soluble in carbon disulfide.



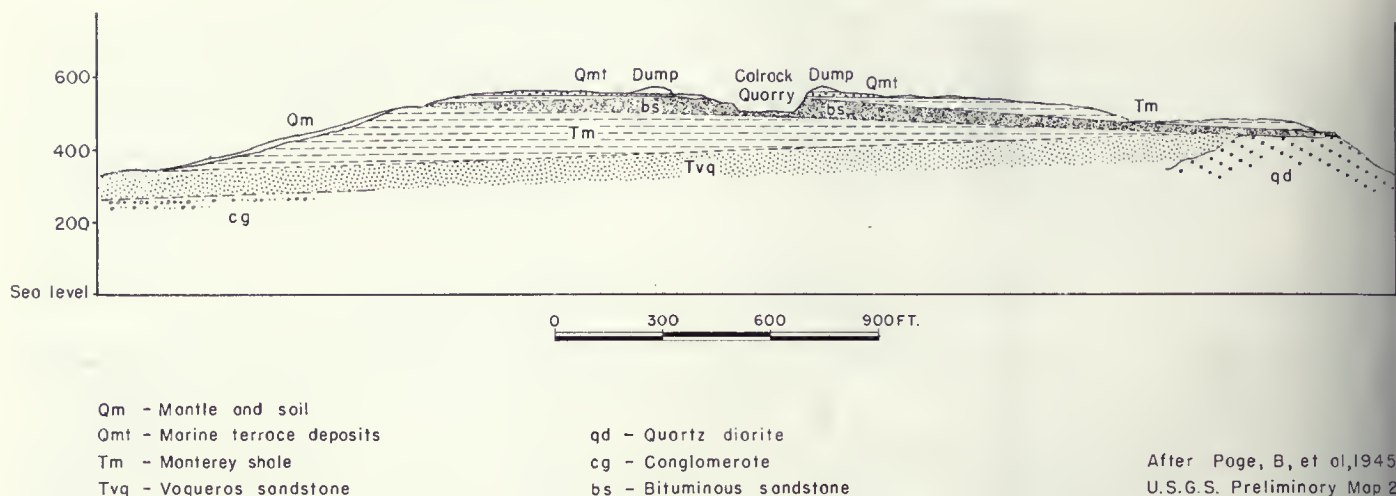


FIGURE 4. Cross section through bituminous sandstone deposits near Santa Cruz.

In the spring of 1955, the Husky Oil Company of Cody, Wyoming, established an experimental project<sup>2</sup> at the Calrock quarry to obtain oil by "cracking" the hydrocarbons contained in the bituminous sandstone. This is done by heating the bituminous sandstone underground, and by condensing the resulting hydrocarbon vapors. The method used is a modification of a Swedish method, developed by Ljungström, which has been used successfully since 1941 on kerogen-type shales.

At the Calrock quarries, holes are drilled through the deposit and into each hole is lowered a special burner using gaseous fuel which heats the hole from about 10 feet from the surface to the bottom. The resulting oil vapors and natural gas are collected, and the oil vapors

<sup>2</sup> The following description is published by permission of the Husky Oil Company, July 25, 1956.

are condensed. The operators anticipate that the natural gas recovered can be used as fuel for the underground burners. In February, 1956, a seven-burner test, two single-burner tests, and a small laboratory were operating. The operators estimated that it would take about a year of further testing with several hundred heating units and a pilot plant before production on a commercial scale could be considered.

*Casmalia, Santa Barbara County.* Bituminous rock deposits occur in an area 5 miles north-northwest of Casmalia and about 15 miles southwest of Santa Maria. These deposits consist of oil-impregnated diatomaceous mudstone and asphalt dikes and sills. They occur mainly in the Sisquoc formation of upper Miocene-lower Pliocene age and form part of a homoclinal structure with beds dipping 20° to 40° NE.



FIGURE 5. Asphalt quarry in the Santa Cruz area showing sill-like intrusion of bituminous rock in diatomaceous shale. Photo by J. F. Newsom, 1901.





FIGURE 6. Photograph showing view of one of the testing areas where the Husky Oil Company is engaged in experiments to recover the oil from bituminous sandstone deposits near Santa Cruz. Compressor, tanks for air and fuel in foreground; laboratory on right; mast for raising and lowering burners into test holes in background.

The oil-impregnated rocks cover about 500 acres. In weathered outcrops the oil-soaked material is soft and the zone does not appear to be more than 10 to 20 feet thick (Williams and Holmes, 1945). The degree of saturation varies but appears to be controlled by the quantity of oil originally available for impregnation, and by the porosity and permeability of the rock. Soft and earthy varieties of the rock have a low oil content, whereas the completely saturated rock is hard and tough.

The asphaltic veins and dikes are distributed over an area about a half mile wide and two miles long. They have the appearance of originating in cracks irregularly disposed through the mudstone and sandstone and range from less than an inch to two feet in width and extend for considerable distances (Eldridge, 1901). Although the veins are irregularly distributed, the prevailing strike seems to be northeasterly and they generally dip steeply to either the northwest or southeast.

Bitumen from the region was used as early as 1885, first as fuel and then, about 10 years later, as paving

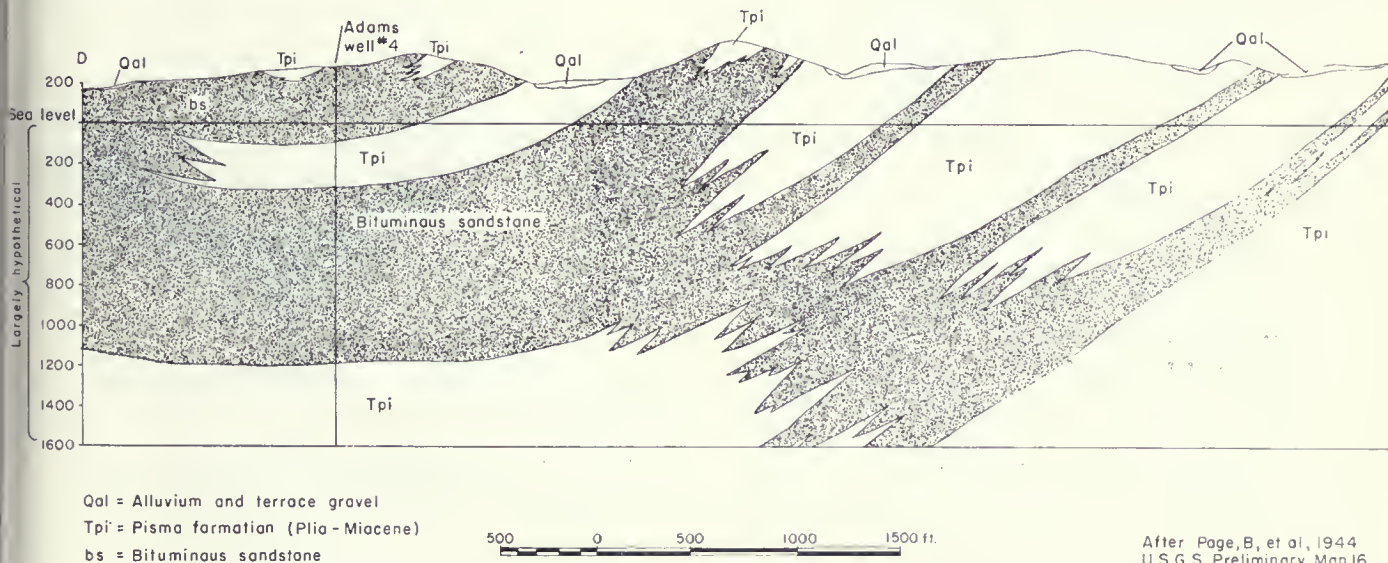


FIGURE 7. Cross section through bituminous sandstone deposits near Edna, San Luis Obispo County.



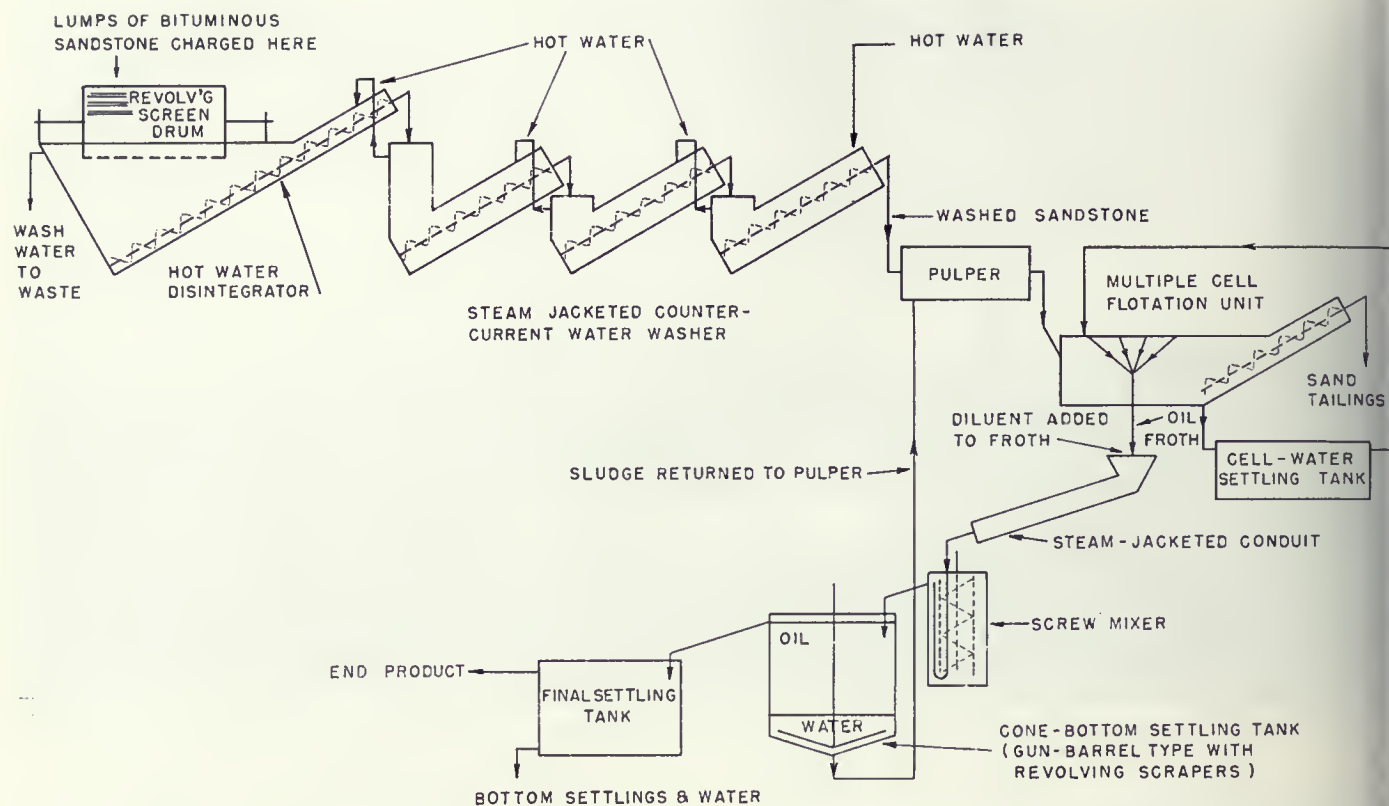


FIGURE 8. Flow sheet of laboratory hot-water separation plant designed to treat Edna bituminous sandstone. After Shea and Higgins, 1945, U. S. Bureau of Mines Rept. Inv. 4246.

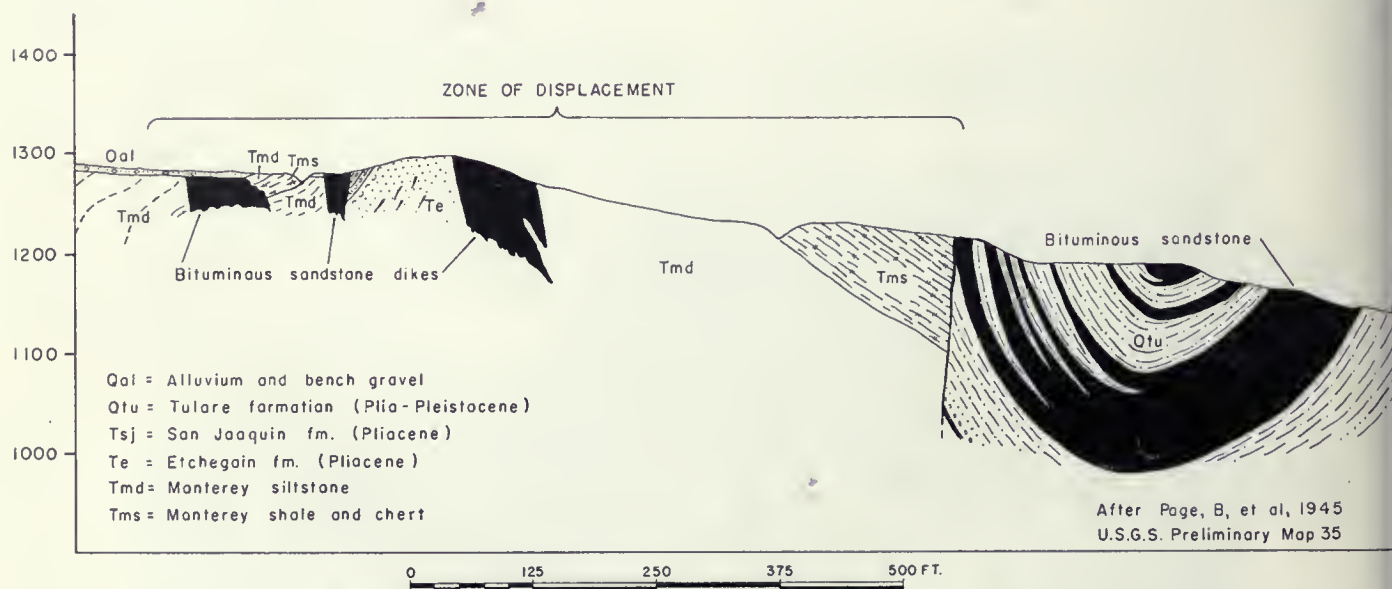


FIGURE 9. Cross section through asphalt and bituminous sandstone deposits in the McKittrick district, Kern County.



material. The first deposits to be worked were the vein deposits, and these were mined largely by underground methods. The largest of these mines, known as the Walcott mine, is reported to have had about 1500 feet of underground workings. The only attempt to utilize the oil-impregnated mudstone was in 1923, when the N.T.U. Company extracted several thousand barrels of oil by destructive distillation (Gore, 1923). But this project was unsuccessful, partly because of difficulties in the extraction process, and partly because of the company's inability to compete with the price of oil from wells. N.T.U. closed its operations in 1928; in 1930 the deposit was investigated by the Los Angeles Bureau of Light and Power as a possible fuel source for power.

Analyses of the oil content of the rocks range from 39 to 82 gallons per ton, and the probable average grade is estimated at 42 gallons (1 barrel) per ton (Williams and Holmes, 1945). Because the oil content of the rock is not uniform, and surface exposures of the bituminous rock are few, no accurate estimate of reserves of the area is possible without extensive core drilling. Surface indications suggest that the oil reserves of the bituminous rock are largely limited to the confines of the N.T.U. quarry which has been estimated to contain about 100,000 barrels (Williams and Holmes, 1945). Additional reserves of considerable magnitude are suggested by outcrops of naturally burned shale south of the N.T.U. mine.

*Edna, San Luis Obispo County.* Bituminous sandstone has been mined from very large deposits near the Edna (Arroyo Grande) oil field 3 to 8 miles south and southeast of San Luis Obispo. These deposits are confined to the Pismo formation of upper Miocene to Pliocene age, which consists of conglomerate, sandstone, diatomaceous sandstone and shale, siliceous shale, and chert. The major structural feature of the region is the Pismo syncline with minor folds superimposed on its flanks. Bituminous sandstone deposits occur on both limbs of the syncline but those on the northeast are the largest. The bituminous outcrops range in quality from black, saturated tar sand to light-brown, slightly bituminous sandstone. Oil probably originated in both the Pismo and underlying Monterey formations and migrated upward along the coarser beds and fractures into the more porous and permeable beds of the Pismo formation, losing its lighter constituents near the surface and leaving asphalt.

Most of the deposits are gently dipping and many large areas of bituminous rocks are exposed with little or no overburden, hence they are favorably situated for surface mining. About 282,880,000 short tons of bituminous material, much of which contains about 11 percent bitumen by weight, or 26 gallons per ton, are estimated to exist in the Edna area (Page et al., 1944). There are 27 quarries, some of which were operated as early as 1887. Eighty thousand tons of bituminous rock were shipped for paving during the period 1887-90, and about 75,000 tons during the period 1890-1915. In 1922, the California Oil Mining Company drove several adits and erected a plant designed to extract oil from the bituminous sandstone by use of solvents (Newman, 1922). The operation was unsuccessful.

In 1943, the Petroleum Field Office of the Bureau of Mines at San Francisco, in cooperation with the U. S.

Geological Survey and the Petroleum Administration for War, initiated a study of bituminous sandstone at Edna. A process for extraction of the oil was developed by the U. S. Bureau of Mines. The studies showed that high recoveries of hydrocarbons, suitable for making fuel oil, diesel fuel, and gasoline, were possible if an especially developed modification of a hot-water separation method was used. The report on these investigations (Shea and Higgins, 1945) includes data on the properties of Edna asphalt and on the distillation analyses of the bitumen, as well as a description of its reduction to coke and a detailed account of the recovery process.

*McKittrick, Kern County.* Abundant deposits of bituminous sandstone, asphaltic alluvium, and asphalt veins and seeps occur along the eastern margin of the Temblor Range just south of the town of McKittrick. Of these materials the bituminous sandstone contains the greatest volume of asphaltic material. The bituminous deposits probably attain a maximum thickness of 80 feet and are most abundant in the Tulare (Plio-Pleistocene) formation; however, the Etchegoin (Pliocene) formation is bituminous locally, and a few bituminous dikes and asphalt seeps occur in the Monterey (Miocene) formation (see fig. 9). The asphalt veins are as much as 100 feet long and range in width from several inches to about eight feet.

Although the area is estimated to contain 8,500,000 to 15,700,000 tons of bituminous material, the smallness and scattered spacing of individual deposits and thick overburden would hinder any large-scale stripping or quarrying operations (Page et al., 1945). The average bitumen content of the deposits in the area is about 10 percent by weight or about 24 gallons per ton. On this basis, the area contains between 4,850,000 and 9,000,000 barrels of accessible bitumen.

Bituminous beds in the McKittrick area were first worked in the early seventies, and the material was sent by wagon to Bakersfield. These veins were prospected and mined extensively and many slumped shafts, adits, and stopes can still be seen.

*Point Arena, Mendocino County.* Bituminous sandstone deposits in the Point Arena area of Mendocino County, about 130 miles north of San Francisco, have been of recurrent interest as a possible source of petroleum and paving material (Holmes, et al., 1951). The deposits were first worked in 1864 when an effort was made to extract the oil by distillation (Weber, 1888, p. 200). This project and later attempts to use the material for paving were of short duration and only a few hundred tons of material were mined.

The bituminous deposits are exposed in Miocene Monterey strata along the steep east flank and south end of an asymmetrical syncline. The principal outcrops are near Arena Cove and a mile to the north on the Porter O'Neal ranch (fig. 10). The main asphaltic bed is believed to extend between these two areas beneath a thin cover of terrace deposits. The largest layer of bituminous sandstone in the Arena Cove area is about 30 feet thick and dips 18° to 30° north. It extends from the sea cliffs eastward about 1650 feet and then swings to the north. The main bituminous sandstone on the O'Neal ranch is about 20 feet thick and dips 50° to 55° SW. Three smaller beds also crop out on the ranch.



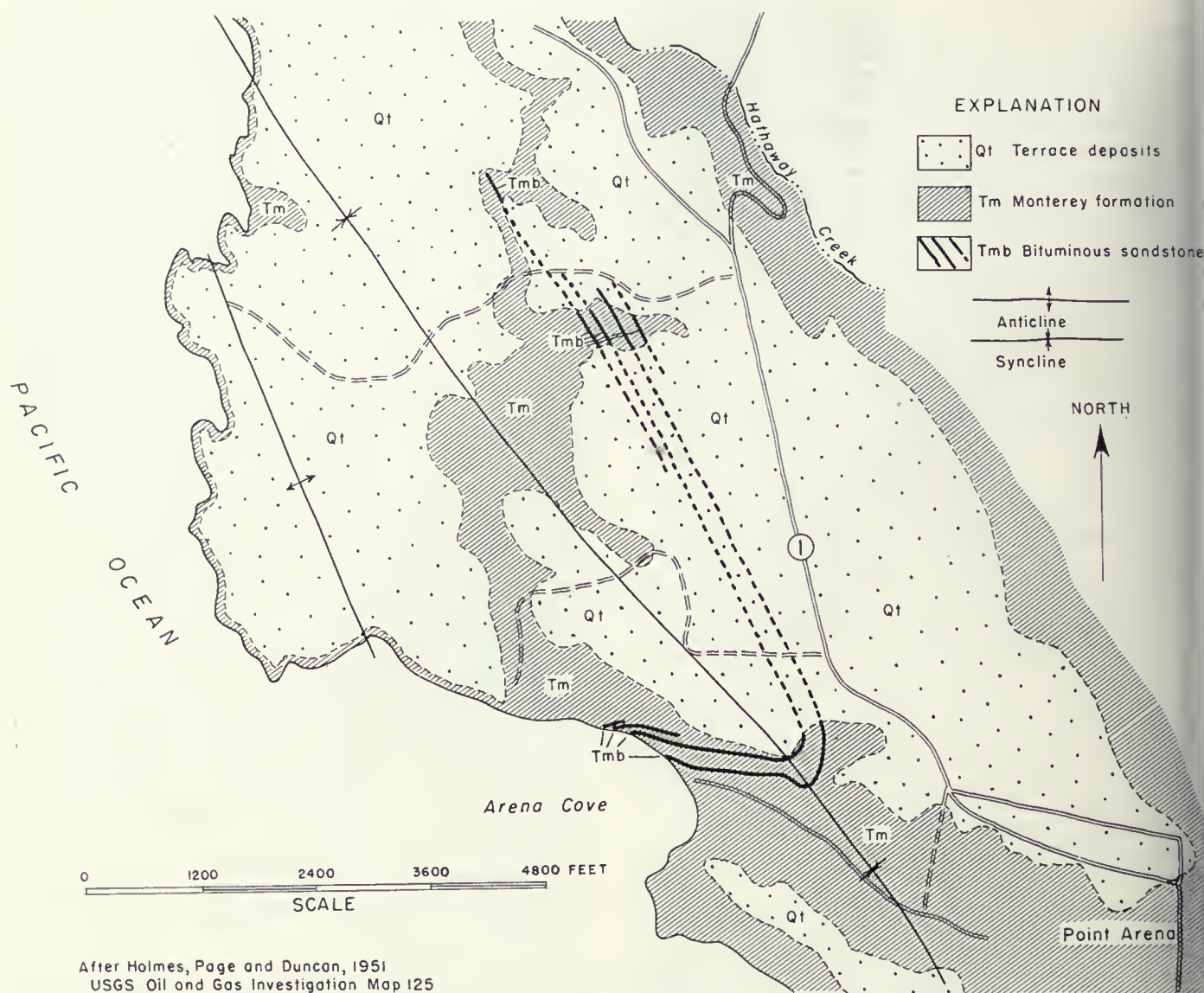


FIGURE 10. Geologic map of bituminous sandstone area near Point Arena and vicinity.

The indicated and inferred reserves of the main bituminous sandstone layer, as projected between the two areas, total about 3,232,000 tons and contain an estimated 1,207,000 barrels of bitumen. Perhaps 60 to 90 percent of this near-surface part of the deposit could be recovered in mining, depending on the methods used. The deposits contain an estimated average of about 6½ percent bitumen by weight or about 15.6 gallons of bitumen per ton.

*Newhall, Los Angeles County.* In an area which lies about 2 miles east and southeast of Newhall in northwestern Los Angeles County and at the west end of the San Gabriel Mountains is a group of small oil fields which includes Elsmere Canyon, Whitney Canyon, Placerita, and the old Placerita schist area (Oakeshott, 1955). Numerous active oil and tar seeps exist in the region and issue from a wide variety of rocks including pre-Cretaceous gneiss and schist, Eocene conglomerate and sandstone, marine Pliocene sandstone, and lower Pleistocene gravel and sandstone. Thinly bedded to massive

bituminous sandstone is extensively exposed in Elsmere and Whitney Canyons, and in an area extending from Elsmere into upper Grapevine Canyon. Most of the bituminous rock is in the lower Pliocene Repetto formation (particularly the basal Pliocene Elsmere member and the middle and upper Pliocene Pico formation). The rocks of the region have been complexly folded and faulted. Penetration of the lenticular cross-bedded sandstone and conglomerate by petroleum has been highly irregular and has been controlled more by structural variations in porosity and permeability than by structure. Though large quantities of bituminous rocks are exposed, no estimates of tonnages or data on amounts of recoverable petroleum have been published.

*Rancho La Brea, Los Angeles County.* The best known of all tar seeps, brea, or asphalt deposits in California is that of Rancho La Brea, in west Los Angeles and adjacent to the abandoned Salt Lake oil field. Lying within a heavily populated area, Rancho La Brea is maintained by the county as a public park. These deposits



osits have yielded one of the most remarkable assemblages of fossils ever found. Live oil springs have fed open ponds of heavy oil which have trapped and preserved a great variety of upper Pleistocene vertebrates including mastodons, ground sloths, horses, camels, saber-toothed tigers, and a host of other forms. Among the many published references to the tar pits is a paper by Cook (1949) which describes the history of the area, the geologic setting, and the forms of life preserved, and contains an extensive bibliography.

#### URANIUM ANALYSES OF CALIFORNIA ASPHALTIC ROCKS

Samples of radioactive asphalt-bearing rocks were collected from several places in California by the U. S. Geological Survey during 1953 and 1954 (Hail, 1954, 1955). Analyses show that uranium is concentrated as an organo-uranium complex in the asphaltic portion of the sample. The uranium contents of the ash of the four richest samples found in California by the U. S. Geological Survey are: Chalona Creek, Monterey County, 0.50 percent U; McKittrick, Kern County, 0.15 percent U; Edna, San Luis Obispo County, 1.9 percent U; Los Alamos, Santa Barbara County, 0.33 percent U. All the deposits, except those in the Chalona Creek area, contain large estimated reserves of asphalt-bearing rock. The average uranium content of samples from the Edna area is 0.376 percent. These analyses apply to the ash of the petroleum content of the rock, and it must be borne in mind that the amount of petroleum ash per ton of bituminous rock is quite small.

Asphalt-bearing rocks from nine other areas in California were sampled and analysed, but did not show significant amounts of uranium. These areas include: Point Arena, Santa Cruz, San Lorenzo Creek, San Ardo, Bradley, Casmalia, Schumann, Gaviota, and Goleta.

#### UTILIZATION AND MARKETS

Sales of bituminous rock in the United States in 1954, according to the U. S. Bureau of Mines, amounted to 300,000 short tons, valued at \$3,700,000. Bituminous limestone from Alabama, Oklahoma, and Texas comprised 90 percent of this total, whereas bituminous sandstone from Missouri, Kentucky, and Oklahoma comprised the balance. Bituminous rock has not been mined commercially in California since the Santa Cruz operations were shut down about 1949.

Gilsonite is mined only in Utah, and in 1954, production amounted to 76,000 short tons, valued at \$2,700,000. Sales value of carload lots of bagged gilsonite per ton at the mine in July 1956 ranged from \$32 to \$38. Selected gilsonite with a fusing point ranging from 270° to 295° F. sold for \$37.00 ton; gilsonite with a 350° F. fusing point sold for \$38.00 ton. "Seconds" with a fusing point ranging from 300°-390° F. were priced at \$32.00 per ton. The hardness and high melting-temperature of gilsonite make it suitable for manufacture of such diversified products as tiles, battery boxes, paints, tanks and insulation compounds.

Production of petroleum asphalt in the United States far outranks that of natural asphalt or bituminous rock. In 1954, a petroleum asphalt production of 14,700,000 short tons amounted to more than 10 times the amount of bituminous rock production. Table 2 shows a comparison of sales of bituminous rock, asphaltite, and petro-

leum asphalt in the United States and California for 1953 and 1954. In California, petroleum asphalt has practically replaced all bituminous rock production since about 1949. The average price of petroleum asphalt per short ton in 1952 amounted to \$18.47 (U. S. Bur. Mines, 1952).

Table 2. Comparison of sales of bituminous rock, gilsonite, and petroleum asphalt in the United States and California (1953-1954),<sup>1</sup> in short tons.

	Year	Bituminous rock	Gilsonite	Petroleum asphalt <sup>2</sup>
United States-----	1954	1,332,000	76,000	14,680,982
	1953	1,440,000	61,000	14,041,648
California-----	1954	0	0	1,378,284
	1953	0	0	1,553,937

<sup>1</sup> Data from U. S. Bur. Mines Mineral Market Report No. MMS 2416, August 1955.

<sup>2</sup> Includes asphalt and asphaltic products manufactured from both domestic and foreign crude petroleum.

About 70 percent of the total petroleum asphalt production is consumed as paving for highways, streets, and airport-runways, and 20 to 25 percent is consumed in roofing manufacture. Table 3 lists the form and uses of

Table 3. Domestic sales of petroleum asphalt in 1952 classified by form and use<sup>1</sup> (value f.o.b. refinery).

Form	Use	Total sales from domestic and foreign petroleum	
		Short tons	Value
Solid and semi-solid products of less than 200 penetration:	Asphalt for		
	Paving-----	5,046,920	\$89,691,204
	Roofing <sup>2</sup> -----	1,790,886	32,879,605
	Waterproofing <sup>3</sup> -----	152,606	3,451,565
	Briquetting <sup>4</sup> -----	140,862	2,329,194
	Molding compounds <sup>5</sup> -----	53,253	1,176,989
	Blending with rubber-----	33,288	838,382
	Pipe coatings-----	28,858	766,551
	Mastic and mastic cake <sup>6</sup> -----	445	15,509
	Miscellaneous <sup>7</sup> -----	413,125	8,122,829
	Total-----	7,660,243	\$139,271,828
Semisolid and liquid products of more than 200 penetration:	Flux <sup>8</sup> for—		
	Roofing <sup>2</sup> -----	808,854	\$11,984,471
	Paving-----	500,002	7,223,034
	Waterproofing <sup>3</sup> -----	15,962	378,487
	Mastic <sup>6</sup> -----	9,367	363,980
	Cutback asphalts <sup>9</sup> (for paving)	3,261,300	62,120,563
	Emulsified asphalt and fluxes <sup>10</sup> -----	128,664	2,846,009
	Paints, enamels, japans, lacquers-----	65,251	1,577,613
	Other liquid products-----	79,631	1,599,999
	Total-----	4,869,031	\$88,094,156
	Grand total-----	12,529,274	\$227,365,984

<sup>1</sup> Data from U. S. Bur. Mines Minerals Yearbook 1952.

<sup>2</sup> Roofing—in manufacture of asphalt shingles.

<sup>3</sup> Waterproofing—for tunnels, building foundations, retaining walls, bridges, culverts, etc., and for constructing built-up roofs.

<sup>4</sup> Briquetting—for binding coal dust or coke breeze into briquets.

<sup>5</sup> Molding compounds—for battery boxes, electrical fittings, push buttons, knobs, handles, etc.

<sup>6</sup> Mastic and mastic cake—for laying foot pavements and floors, waterproofing bridges, lining reservoirs and tanks; capable of being poured and smoothed by hand troweling.

<sup>7</sup> Miscellaneous—such as dips, acid resisting compounds, putty, saturated building paper, fiber board and floor coverings, etc.

<sup>8</sup> Flux—used in softening native asphalt or solid petroleum asphalt.

<sup>9</sup> Cutback asphalts—asphalts softened or liquefied by mixing them with petroleum distillates and used for hot-laid road paving.

<sup>10</sup> Emulsified asphalt and fluxes—asphalts and fluxes emulsified with water for cold-patching roads, road laying, in portland cement concrete mixes to give it waterproofing and salt corrosion resistance, in adobe bricks, in paper-sizing.



petroleum asphalt and the amount of sales of each item for 1952.

Improved refining processes have given the asphalt technologist dependable materials of a quality and uniformity much superior to products 20 years ago. The discovery that the blowing of air through asphalt at high temperatures would give the asphalt a higher melting point led to the production of asphalt products which could be used for waterproofing sloping roofs. One of the newest developments in the asphalt trade is the use of special, catalytically treated asphalt in the lining of canals. Hot asphalt is sprayed to form a thick layer, and six to twelve inches of earth or gravel are filled back over this membrane. Asphalt emulsified in water has led to an entire line of speciality uses such as: in portland cement concrete mixes to give waterproofing and salt corrosive resistance; in adobe bricks for decorative building uses; and as a paper-sizing for packaging supplies.

Imports of petroleum asphalt into the United States in 1953 amounted to approximately 460,000 short tons valued at \$5,200,000. Most of this came from the Netherlands Antilles. A small amount of liquid petroleum asphalt came from Venezuela. Imports of natural asphalt and bitumens amounted to only 2,699 short tons in 1953. This was mostly lake asphalt from Trinidad and was valued at \$71,000. Exports of petroleum asphalt and its products from the United States in 1954 amounted to 291,000 short tons. The countries to which major shipments were made in decreasing order of amount were: Indo-China, Canada, Philippines, Brazil, India, and Union of South Africa.

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## BARITE

By CHARLES J. KUNDERT

Occurrences of barite are widespread in California and the mineral has been produced commercially at several localities. From 1910 to 1952 approximately 540,000 tons of barite valued at about \$3,650,000 have been mined in the state. In recent years the annual consumption of barite in California has been in the range of 30,000 to 100,000 tons. This is approximately one-tenth of the barite produced annually in the United States. At present this demand is being supplied almost entirely by operators of barite deposits in Nevada.

**Geologic Occurrence.** Barite ( $\text{BaSO}_4$ ) is the most common barium mineral. Its principal industrial uses stem from its relatively high specific gravity (4.3-4.6) and its chemical inertness. Witherite ( $\text{BaCO}_3$ ) is much less common than barite. Although barium-bearing feldspars have been noted, barium ordinarily is not a primary constituent of igneous rocks. Commercial deposits of barite occur as (1) residual deposits derived from barite-bearing rocks, (2) replacements of limestone, dolomite or shale, and (3) fracture fillings. Most of the barite produced in the United States has been obtained from residual deposits in Missouri and from shale-replacement deposits in Arkansas. All of the sustained production of barite in California has been obtained from bodies that have apparently replaced limestone or from bodies that have filled fractures. A minor tonnage of barite has been mined from a residual deposit in California.

A mine in Arkansas has been the principal source of barite in the United States since 1945. The barite is being produced from a synclinal replacement deposit near Magnet Cove. Carbonate-rich zones at the base of the Pennsylvanian Stanley shale apparently have been replaced by barite. The ore zone is about 35 to 45 feet thick and averages about 67 percent  $\text{BaSO}_4$ . It is being mined by both underground and surface methods. The ore is beneficiated to meet specifications. In January 1949, this deposit was estimated to contain 8,400,000 tons of reserves (Dean and Brobst, 1955, p. 173).

During the period 1901 to 1951, 5,219,260 tons of barite were produced in Missouri. Most of the barite has been recovered from residual clay derived from Cambrian Potosi dolomite. The dolomite originally contained barite in the form of fracture and cavity fillings, and weathering of the dolomite left the relatively insoluble barite dispersed in residual clay. The deposits are strip-mined and hauled to washing plants for concentration.

In 1952, 68,062 tons of barite were produced in Nevada. An area near Battle Mountain has been the source of most of the production. The major deposits in this area have partly replaced limestone along shear zones. The mines are exploited by open pit methods. Some of the ore has to be up-graded by screening. These deposits have been estimated to contain at least  $2\frac{1}{2}$  million tons of barite (Arundale, 1956, p. 89).

**California Barite.** Barite is a very common gangue mineral in vein deposits and occurs widely throughout the state (Murdoch and Webb, 1948, p. 64). The accompanying map shows the locations of barite mines in the state that have yielded recorded quantities of barite. The five mines marked with an X have contributed most

of the barite mined in California. Of these five, the El Portal mine in Mariposa County has yielded approximately 400,000 tons or about three-fourths of the total production. Two of the smaller mines yielded about 17,000 to 20,000 tons of barite, and two had a recorded total yield of about 35,000 tons. All of these five deposits occur in the Calaveras formation of Carboniferous(?) age in the Sierra Nevada.

The deposit near El Portal, Mariposa County, which is reported to have been discovered and first mined in the 1880's, (Fitch, 1931, p. 461) is unusual in that it has also yielded commercial quantities of witherite. The barite-witherite bodies appear to have replaced limestone layers in an isoclinally folded sequence of metasedimentary rocks that are part of the Calaveras formation of Carboniferous(?) age. The ore bodies are as much as 20 feet thick and have been traced for 3 miles. They have attitudes parallel to those of the enclosing metasedimentary rocks which strike about north and dip steeply.

Apparently, the barite deposits were formed by replacement of beds of limestone by barium-bearing minerals derived from solutions that originated in the magma that formed underlying granitic rocks. The contact between granite and metasedimentary rock lies to the north. The barite deposits, in a distance of about 1 mile along the strike grade from barite to witherite to crystalline limestone to calc-silicate rocks at the contact. Three barite bodies are known: two of them have been mined. Both of these are exposed in the walls of the west-trending canyon of the Merced River. The eastern body has been mined mostly north of the river and the western body has been mined wholly south of the river. Underground mining methods have been used most in the development of the mine. The mined material was white and granular, averaged about 80 percent  $\text{BaSO}_4$  and 20 percent silica, and had to be beneficiated to meet specifications. The mine was active almost continuously from 1910 to 1948. It has been inactive since 1948.

About 70,000 tons of barite have been produced in Nevada County. During the 1920's the Democrat mine near Alta was the principal source of barite in the state. The mine workings consist of a large open-cut about 200 feet long, 50 feet wide, and 30 feet deep. The open-cut is parallel to the trend of the barite veins which strike N.  $5^\circ$  E. and dip  $65^\circ$  to the west. The barite veins apparently occur as bedding plane fracture fillings in deeply weathered metasedimentary rocks of the Calaveras formation. Two veins are exposed: the western vein is about 30 feet wide and was the main source of the ore; the eastern vein is about 7 feet wide. The wall rock has been altered near the contacts with the barite veins, and the veins are brecciated near the contacts. Most of the barite remaining in the deposit is granular and dark gray. About 35,000 tons of barite have been shipped from this mine. The deposit has been idle since 1930.

The Spanish mine near Graniteville, Nevada County, was worked from 1930 to 1945 and reopened in 1955. It yielded about 35,000 tons of barite previous to 1955. Two veins of barite, which are as much as 3 feet thick, are exposed at the surface. They strike about N.  $5^\circ$  W.



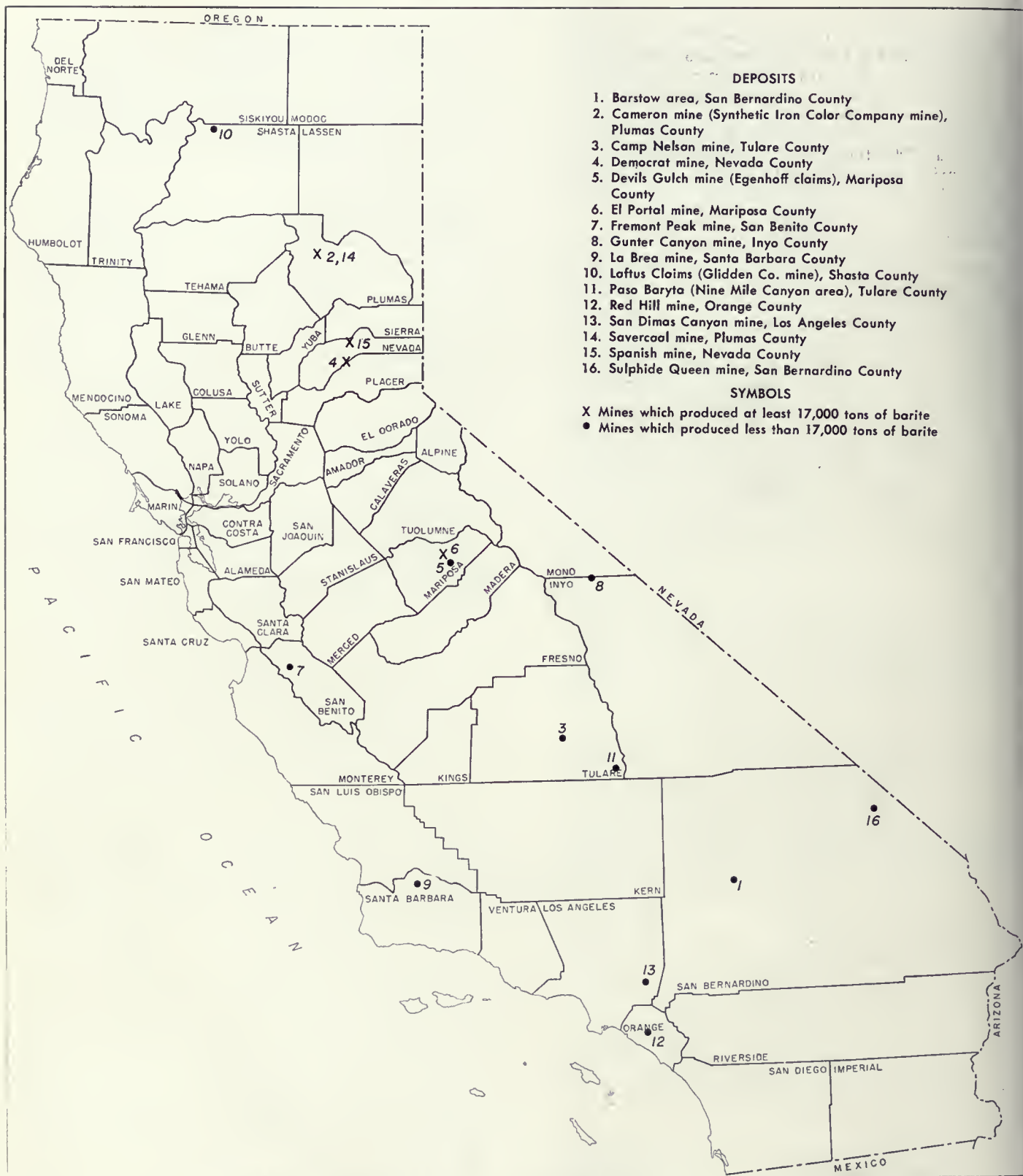


FIGURE 1. Index map of California showing locations of barite deposits with recorded production.

and dip 30° east in apparent conformity with attitudes of surrounding metasedimentary rocks of the Calaveras formation.

The barite veins are brecciated near the contacts with the enclosing metasedimentary rocks. In the period 1930 to 1945 the barite was mined by underground methods.



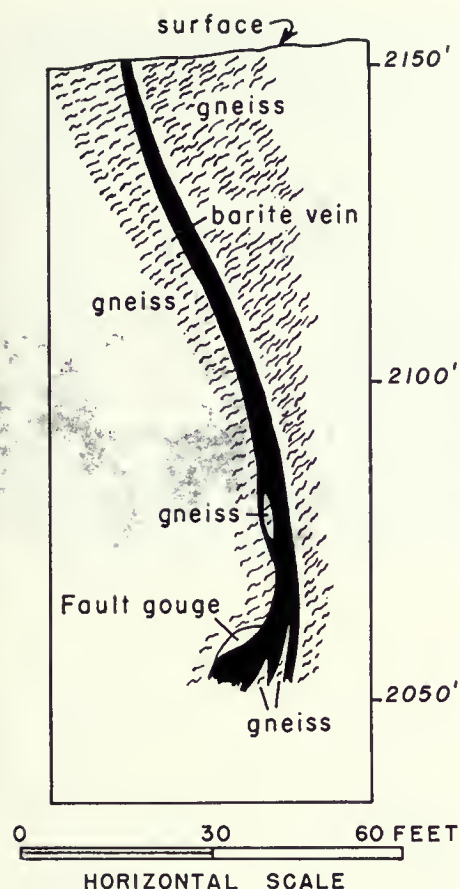


FIGURE 2. Cross-section of typical barite vein at the Barium Queen mine, Barstow area, San Bernardino County. After Durrell, C., 1954.

Apparently the two veins joined at depth and increased in thickness to as much as 12 feet. In 1955 the barite was mined by open pit methods. As exposed at a depth below the former surface of about 100-150 feet, the barite body is about 12 feet thick and has a strike length of about 75-100 feet. It dips 45 degrees to the east and strikes N. 10° E. It was being mined in benches, each bench being about 6-10 feet high. The barite was crushed to minus 1 inch at the mine, and trucked 41 miles to the railroad at Colfax.

The Synthetic Iron Color Company mine near Greenville, Plumas County, yielded about 17,000 tons of barite from 1932 to 1936. The barite was obtained from a lenticular body which measured about 175 feet long, as much as 30 feet wide, and about 60 feet in down-dip dimension. The lens had a north strike and dipped 45° to 60° to the west. It was composed of white, granular barite and apparently occurred as a limestone-replacement body. Horseshoes of limestone and quartzite were encountered during mining of the lens (oral communication, Donald R. Irving, 1953). The mine was developed by both open pit and underground methods.

The Synthetic Iron Color mine is adjoined to the south by the Savereool mine which operated from 1946 to 1953 and yielded about 20,000 tons of barite. The barite occurs as a lenticular body which has replaced limestone in Calaveras slate. The lens and the surrounding rocks strike N. 30° W. and dip 65° to the southwest. The

barite body was from 8 to 12 feet wide and 300 feet or more long, and measured at least 60 feet in a down-dip dimension. It was mined by underground methods.

The Nevada and Plumas County mines described in the preceding paragraphs were high-grade deposits. In general the ore averaged from 96 to 99 percent  $\text{BaSO}_4$  with an extremely low iron oxide content. Thus despite the small size of the deposits, relatively costly mining methods, and accessibility of the deposits, they were commercial because of the high proportion of barite.

Minor production of barite has been recorded from the following properties: Barstow area, San Bernardino County; Camp Nelson barite mine, Tulare County; Devils Gulch mine (Egenhoff claims), Mariposa County; Fremont Peak mine, Monterey County; Gunter Canyon mine, Inyo County; La Brea mine, Santa Barbara County; Loftus claims (Glidden Company mine), Shasta County; Paso Baryta mine (Nine Mile Canyon area), Tulare County; Red Hill mine, Orange County; San Dimas Canyon mine, Los Angeles County; Sulphide Queen mine, San Bernardino County. Most of the barite at these properties occurs as limestone-replacement or fracture-filling bodies which are sufficiently rich to be mined for their barite content alone. Barite at the Camp Nelson mine occurs as residual deposits concentrated by weathering and erosion of baritic-limestone of the Calaveras (?) formation. Barite from the Sulphide Queen mine has been produced as a by-product from the concentration of rare-earth minerals which occur in barite-carbonate-quartz veins. A portion of production from the Barstow area has come from reworked tailings piles of barite-silica veins which were mined and milled for their silver content in the late 1890's and early 1900's.

The influx of great quantities of barite into California from Nevada has hindered barite mining in California. Most of the Nevada barite has been obtained from open-pit operations of limestone-replacement deposits of considerable size. Despite a freight rate of about \$6.00 per ton, the shipment of barite from Nevada to California has proved economical because of the quality and quantity of the deposits and the ease with which they are mined.

In past years barite deposits containing 17,000 tons or more of 96 percent  $\text{BaSO}_4$  have had sustained commercial production. Smaller deposits have yielded barite in limited quantities when the demand was great and the price was high.

Three mines were yielding small quantities of barite in 1954; the Camp Nelson barite mine, a mine in the Paso Baryta area, and a mine in the Barstow area. Barite from the mine in the Barstow area was stockpiled at the mine. Barite from the other two mines was utilized in oil-well drilling fluids and as fillers.

In 1955 the Spanish mine was reopened. It was mined by open pit methods and the barite produced was utilized in oil-well drilling fluids. The mine was closed in the late fall of the year.

Late in 1956, the Nine Mile Canyon deposit was reopened and the barite was being concentrated by jigging in a mill at Linnie Station.

**Utilization and Markets.** In 1953 the barite consumed in the United States totaled about 1,135,862 tons. The oil-well drilling mud industry consumed 72 percent,



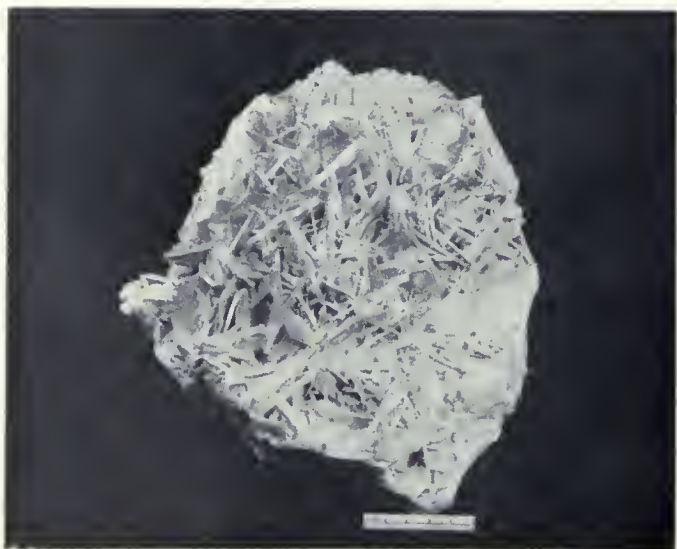


FIGURE 3. Coarsely crystalline barite from Barium Queen mine, Barstow area, San Bernardino County. Scale is 5 cm long. Photo by Mary Hill.

14 percent was used in the manufacture of barium chemicals, and 4 percent was used in the manufacture of lithopone, a white pigment composed of approximately 70 percent barium sulfide and 30 percent zinc sulfide. The remaining 10 percent was used in the manufacture of glass, as a filler in paint and rubber, as a dense aggregate in concrete, and other miscellaneous uses (Arundale, 1956, p. 89).

Approximately 60 to 70 percent of the 100,000 tons of barite consumed annually in California is used in oil-well drilling muds. Principally because of its inertness, high specific gravity, and relatively low cost, barite is used as a weighting agent in drilling muds when abnormal gas and oil pressures must be contained. The crude ore is shipped to grinding plants, ground so that 95 percent passes 325 mesh, and bagged. Some of the grinding plants require crude barite no greater than 1 inch in diameter. A specific gravity of 4.2 is the principal specification for barite used in drilling fluids. Specifications for color, iron content, and content of  $\text{BaSO}_4$  are flexible if 4.2 specific gravity can be attained.

The chemical industry consumes the bulk of the remainder of the barite used in California. In general, barite with a minimum of 94 percent  $\text{BaSO}_4$ , a maximum of 1 percent iron, and no more than a trace of fluorine is accepted as chemical grade. Crude barite is brought to the industry, ground to 80 mesh, and processed to make barium chemicals. Barium oxide, peroxide, hydrate, nitrate, sulfide, sulfate and carbonate and sodium sulfite and polysulfide are produced by the barium chemical industry in California.

Minor quantities of barite are consumed in the glass and filler industries. Glassmakers usually specify a material containing a minimum of 98 percent  $\text{BaSO}_4$ , maximum  $\text{SiO}_2$  0.15 percent,  $\text{Al}_2\text{O}_3$  0.15 percent, and  $\text{Fe}_2\text{O}_3$  0.15 percent. Usually the color-conscious filler industry requires a white material as well as one of chemical grade.

Prices for crude barite in California have fluctuated from a low of about \$1.50 per ton in 1914 to the current



FIGURE 4. Typical barite-silica vein material from the Barstow area, San Bernardino County. Bladed crystals are barite. Scale is 5 cm long. Photo by Mary Hill.

level of \$14.00 to \$16.00 per ton for 90 to 98 percent  $\text{BaSO}_4$  delivered to grinding plants. The average price has been about \$6.00 per ton. A large percentage of the barite produced in California has been obtained from operations controlled by the consumers, and therefore the true market value for crude barite is difficult to establish. Barite ground to 325 mesh for use in oil-well drilling fluids sells for approximately \$40.00 per ton at the utilization centers. If it has been bleached for use in paint, glass, or as fillers, the cost is about \$8.00 a ton higher.

Oil-well drilling fluid companies, barium chemical companies, and industrial mineral grinding plants are potential buyers of crude ore. Most of these companies desire ore not greater than 1 inch in diameter, though some use lump ore as much as 10 inches in diameter.

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## BERYLLIUM

By LAUREN A. WRIGHT

The mineral beryl, which is the only commercial source of beryllium metal, is widely but very sparsely distributed in pegmatite bodies in southern California, and has been mined as a gem stone at some of them. One of the beryl deposits in California has yet proved rich enough to be mined as a source of beryllium.

Most of the beryl that is consumed domestically is brought into the United States from foreign sources. The metal, which has several unusual properties and numerous useful applications, is employed mainly as an alloy.

**Mineralogy and Occurrences.** Beryl ( $\text{Be}_3\text{Al}_2(\text{Si}_6\text{O}_{18})$ ) occurs as hexagonal crystals and as irregular masses, is transparent to subtranslucent, and generally is colored green or blue; less commonly it is colorless, pale yellow or pale rose. It has a glassy to distinctly greasy luster, a conchoidal to uneven fracture, a hardness of 7.5-8 (Mohs' scale), and a specific gravity of 2.6 to 2.8. It closely resembles quartz, but in general shows more color and a more greasy luster than the colorless to milky quartz with which most beryl is associated. Although a BeO content of 14 percent characterizes theoretically pure beryl, the mineral generally contains 10 to 12 percent BeO, as alkalis commonly substitute for some of the beryllium. Other beryllium-bearing minerals exist (e.g. phenacite ( $\text{Be}_2\text{SiO}_4$ ), chrysoberyl ( $\text{BeAl}_2\text{O}_4$ ), helvite ( $\text{R}_4\text{Be}_3\text{Si}_3\text{O}_{12}\text{S}$ ), gadolinite ( $\text{Be}_3\text{FeY}_2\text{Si}_2\text{O}_{10}$ ), and berylmonite ( $\text{NaBePO}_4$ ), but none of these constitutes a present commercial source of beryllium.

Beryl generally occurs as a primary constituent of granitic pegmatite bodies. It also exists, although much less abundantly, in veins and disseminations (most of which appear to be genetically related to pegmatite bodies) and in certain occurrences of finer grained granitic rocks. Beryl is uncommon, and even pegmatite that is a commercial source of beryl rarely contains more than 1 percent of the mineral.

Beryl occurs in various places in the pegmatite bodies, but the larger crystals and masses generally have been found in the interior parts. At a few localities, beryl masses of many tons have been encountered, but the beryl recovered in most operations consists of crystals and masses within the range of 1 inch to 18 inches in diameter. Smaller grains of beryl are rather evenly distributed through large parts of some pegmatites, but deposits of this type are uncommon. The commercial recovery of this finer grained beryl awaits the development of a successful method of beneficiation.

A pegmatite district in the Black Hills of South Dakota (Page and others, 1953), has been the principal domestic source of beryl. The largest of the known domestic reserves exist in the tin-spodumene belt of North Carolina (Griffitts, 1954), but the beryl in these deposits is generally too fine-grained to be concentrated by hand. Since 1951, the most productive single operation for beryl in the United States has been the Harding mine, northern New Mexico, where huge beryl masses, each containing several tons to several tens of tons of nearly pure material, have been developed. Beryl also has been recovered from pegmatites in at least 13 other states.

Domestic sources, however, have yielded no more than a few hundred tons of the several thousand tons of beryl ore that has been purchased annually in the United States in recent years. Considerably more than half of the free world's output is obtained from pegmatites in Brazil, Southern Rhodesia, and Argentina.

Of the known non-pegmatite occurrences of beryllium in the United States the helvite-bearing contact metamorphic deposits at Iron Mountain, southwestern New Mexico (Jahns, 1944), probably are of the greatest commercial interest. These contain reserves estimated at 184,000 tons that average about 0.2 percent BeO, and 4,500 tons that averages about 0.7 percent BeO, but the economic extraction of the beryllium remains an unsolved problem. As the helvite at this locality previously had been mistaken for garnet, one should not discount the possible existence of previously undetected helvite and associated beryllium-bearing minerals in contact metamorphic deposits that occur in California and elsewhere.

**Localities in California.\*** Beryl has been noted in a large number of the pegmatite dikes in California, but from none of them has it been recovered commercially except as a gem stone (see section on gem stones in this volume). Moreover, only a very small part of the beryl content of the pegmatites is of gem quality. Among the more beryl-rich pegmatites in the state are those of western Riverside County, but even these have not been shown to contain more than a small fraction of 1 percent of the mineral.

Most of the observed beryl in California occurs as well-formed crystals associated with coarse pegmatite in the interior zones of the dikes, but anhedral masses of beryl have locally formed in the wall zones. Most of the beryl in any one of the pegmatite bodies is confined to a single zone. Most of the beryl crystals and masses are colored pale green to pale blue, and range from a small fraction of an inch to several inches in maximum dimension.

Beryl-bearing stringers have been noted at localities 5 to 6 miles east of Lone Pine in the Owens Valley region of Inyo County. These stringers seem to be genetically related to nearby pegmatite bodies, and, indeed, many appear to be composed of fine-grained pegmatitic material. Most of them are enclosed by ordinary granitic rocks. The stringers exist as fracture-fillings mostly  $\frac{1}{16}$  inch to 4 inches thick, and consist of muscovite, quartz, and beryl, with or without epidote and fluorite. In general, they are so widely spaced as to preclude a large-tonnage removal of rock that would average more than 0.2 percent beryl.

Very small percentages of beryllium have been noted in spectrographic analyses of samples from taconite bodies and associated igneous rocks in the Pine Creek and Tungsten Hills area of Inyo County.<sup>1</sup> In the late 1940's,

\* Much of the information in the following discussion has been kindly furnished by Dr. R. H. Jahns, Professor of Geology, California Institute of Technology.

<sup>1</sup> The information in this and the following paragraph was kindly furnished by Wallace R. Griffitts, Geologist, U. S. Geological Survey.



the U. S. Geological Survey sampled, in a preliminary manner, such rocks at several tungsten properties in this area. The samples, about 46 in number, ranged from less than .0001 percent to .0045 percent in BeO. Those from the Little Sister and Pine Creek mines were consistently the highest in BeO, but averaged only about .0002 percent. Lower BeO averages were shown in analyses of samples from the Aeroplane (Moonlight) and Round Valley mines and the Yancy prospect. Two tailings samples from the Tungstar mine—one from an older pile and another from a younger pile—contained .0058 and .0021 percent BeO respectively.

The form in which the beryllium occurs in these deposits has not been determined. In the taconite bodies it probably is dispersed through the common silicate minerals, and, therefore, would have to be separated chemically rather than mechanically. If beryllium or a beryllium-bearing mineral could be concentrated, even as a by-product, the lowness of the grade would still make the procedure non-economic with respect to the present price of beryllium.

*Mining Methods and Treatment.* Most commercial beryl has been recovered as a by-product or coproduct of other pegmatite minerals from which it ordinarily is hand-cobbed. Such minerals are recovered in both underground and surface operations. As a minimum of 8 percent BeO generally is specified by purchasers, and as the price per unit increases with increasing BeO content, the sorting must be very carefully done.

An economic method for the recovery of beryl that is too fine-grained to be hand sorted has been sought since the early 1940's, mainly in the laboratories of the U. S. Bureau of Mines. A flotation method (Runke, 1954) has proved moderately successful on an experimental basis, but in 1955 beryl beneficiation remained to be placed on a commercial scale.

Beryllium is now recovered by a procedure that involves (1) the production of beryllium oxide from beryl, (2) the dissolving of beryllium oxide in an aqueous solution of acid ammonium fluoride, (3) a heating of the resulting ammonium beryllium fluoride from a beryllium fluoride residue, and (4) a reduction of this residue, with a stoichiometric deficiency of magnesium, in a graphite-lined furnace at about 1300 degrees C. The oxide generally is produced by either of two methods. In one, fine-ground beryl is sintered with sodium ferrie fluoride at about 750 degrees C.; sodium beryllium fluoride is water-leached from the sintered cake; and beryllium hydroxide is precipitated when sodium hydroxide is added to the solution. In the other method, the beryl is fused at about 1625° C. and quenched in water to form a glass which is then ground, mixed in sulfuric acid and heated. Beryllium and aluminum silicates are then leached with water, the aluminum is converted to ammonium alum, and beryllium hydroxide is precipitated with the addition of sodium hydroxide. The beryllium hydroxide, thus produced by either method, can be ignited to form beryllium oxide or can be used in the preparation of other beryllium compounds.

The production of beryllium and beryllium compounds in the United States centers almost entirely about plants east of the Mississippi River. No beryllium-processing plants are in California.

*Utilization.* Beryllium is a useful metal mainly because it has a low specific gravity (about 1.8), a high modulus of elasticity (about 40,000 psi), and a high melting point (1285° C.), and because it serves as a hardening and strengthening agent in various alloys. In recent years from 80 to 90 percent of the beryllium consumed domestically has been used in alloys, especially beryllium-copper alloys to which 83 percent of the nation's beryl consumption was channeled in 1953. Copper that is alloyed with about 2 percent beryllium and heat treated is about 6 times stronger than pure copper. Copper-beryllium alloys are used in such articles as bushings, shims, contact points, current-carrying springs, and non-sparking tools. Other beryllium-bearing alloys include beryllium-zinc, ticonium (Be-Ni-Co-Cr-Mo), beryllium-nickel, beryllium-platinum, beryllium-steel, beryllium-aluminum, and beryllium magnesium, but their use has been very limited.

At ordinary temperatures beryllium metal is very brittle and unsuited to cold-working. This property, which is possibly attributable to traces of impurities, has hindered the use of the metal. It can be worked, however, at temperatures above 800°C. As beryllium has a high X-ray transmission factor, thin plates of the metal are used in X-ray tube windows. In the atomic energy field, it is used as a moderator and reflector of neutrons emitted during the fission of U-235 and plutonium, and for other purposes for which data are restricted by security regulations. In mid-1956, the U. S. Atomic Energy Commission contracted with the two large domestic producers of beryllium for 1,000,000 pounds of reactor-grade metal to be delivered over a 5-year period.

As beryllium oxide has high dielectric strength through a wide range of temperatures, and high resistance to thermal shock, it has an important but limited use as a refractory in small, high temperature electric furnaces and nuclear power plants, as well as in porcelain for aircraft spark plugs and ultra-high-frequency electrical insulators. The oxide also has numerous other minor applications.

The most-used beryllium salt is beryllium nitrate which is employed with thorium nitrate in incandescent gas mantles. Beryllium chloride, sodium-beryllium fluoride, and beryllium halides have very minor applications.

*Markets and Prices.* More than 90 percent of the domestic output of beryllium metal, alloys and compounds are produced by two companies—the Beryllium Corporation, Reading, Pennsylvania; and the Brush Beryllium Company, Cleveland, Ohio. These companies and the General Services Administration constitute the principal markets for beryl ore in the United States, although relatively small amounts of the mineral are purchased by other manufacturing concerns (see recent editions of Minerals Yearbook), and by mineral brokers.

Since early in 1953, the quoted price (E. & M. J. Metal and Mineral Markets) for domestic beryllium ore, f.o.b. mine, Colorado, has remained at \$46 to \$48 per short ton unit of BeO contained in 10 to 12 percent ore, but much higher prices commonly have prevailed in actual sales during this period.





FIGURE 1. Specimens of green prismatic beryl in quartz from the El Molino gem mine, Pala district, San Diego County. Larger specimen is about 3 inches across. *Photo by Richard H. Jahns.*

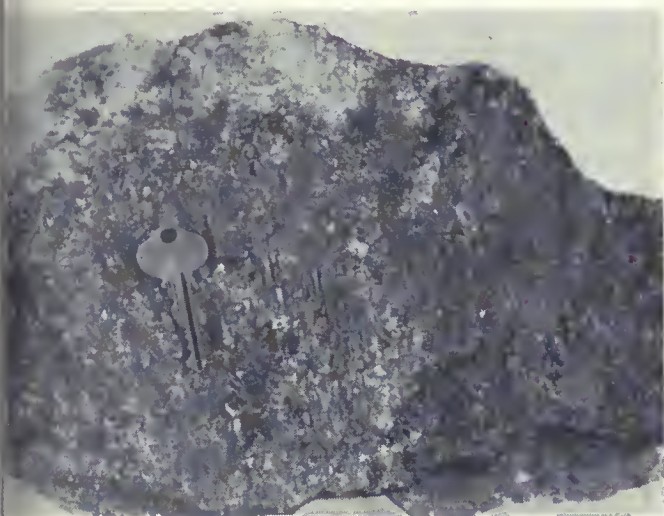


FIGURE 2. Specimen, showing surface of beryl-bearing vein, from a locality about 6 miles east of Lone Pine, Inyo County. Beryl (dark prisms) and muscovite (dark flakes) occupy vein in granitic country rock. *Photo by Richard H. Jahns.*

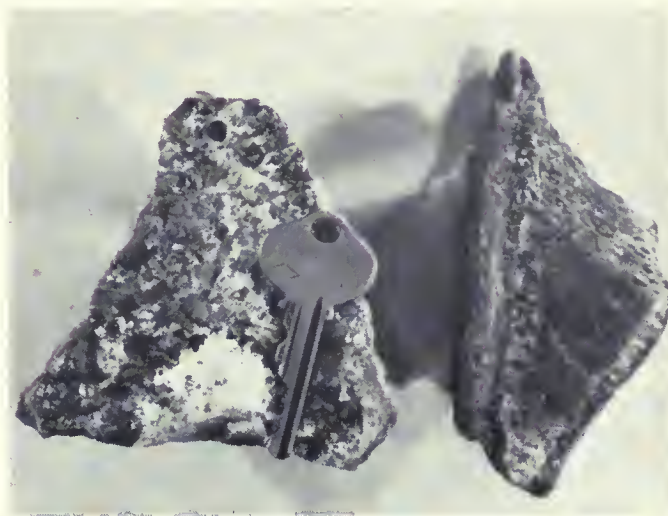


FIGURE 3. Specimens, showing surface (left) and sections (right) of beryl-bearing vein, from same locality indicated in figure 2. Beryl is medium-dark material on surface of left specimen and near vertical edges of right specimen. The very dark vein-forming material is muscovite. *Photo by Richard H. Jahns.*



In 1952, the General Services Administration instituted a purchase program for domestically produced beryl ore, containing not less than 8 percent beryllium oxide by weight, to be purchased from producers whose annual output does not exceed 25 short tons. This program originally was scheduled to extend until June 30, 1955, or until 1,500 tons had been delivered, whichever occurred first. It has since been extended until June 30, 1962 or until 4,500 tons has been purchased. The program provides for the purchase of shipments, on the basis of visual inspection by the federal government, at the rate of \$400 per short dry ton. The following rates apply to sampled and analyzed ore: 8 to 8.9 percent inclusive, \$40 per unit; 9 to 9.9 percent inclusive, \$45 per unit; 10 percent and over, \$50 per unit. Persons desiring to participate in this program should first communicate with the G.S.A. Beryl mined in California and sold to the G.S.A. probably would be purchased at the nearest beryl depot, which is in Custer, South Dakota. Although beryl is one of the minerals for which exploration loans may be granted by the Defense Minerals Exploration Administration, no loans in this category had been granted in California by mid-1956.

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## BISMUTH

By CHARLES W. CHESTERMAN

The total production of bismuth in California has been limited to about 20 tons of bismuth ore produced at a copper mine in Riverside County in 1904. Therefore, in order to meet current demands of the metallurgical and pharmaceutical industries, bismuth and bismuth compounds must be brought into the state.

**Mineralogy.** Native bismuth and bismuthinite are the two important minerals of bismuth. Native bismuth is sectile, brittle, has a metallic luster, a silver-white color with a reddish hue, and occurs associated with ores of cobalt, nickel and silver. Bismuthinite ( $\text{Bi}_2\text{S}_3$ ) is somewhat sectile, has a metallic luster, lead-gray to tin-white in color, hardness of 2 (Mohs' scale), specific gravity of 9.4-9.5, and contains, when pure, 81.2 percent bismuth.

Other bismuth minerals, which occur as alteration products of native bismuth and bismuthinite are: bismite (bismuth ocher,  $\text{Bi}_2\text{O}_3$ ), 96.6 percent bismuth; bismutite ( $\text{Bi}_2\text{O}_3 \cdot \text{CO}_2 \cdot \text{H}_2\text{O}$ ), 80.6 percent bismuth, and bismutospharite ( $\text{Bi}_2(\text{CO}_3) \cdot 2\text{Bi}_2\text{O}_3$ ), 81.9 percent bismuth.

**General Geology.** Bismuth minerals are ordinarily associated with minerals that contain other metals such as copper, gold, lead, silver, cobalt, nickel and tin. The bismuth minerals occur in many types of vein deposits and in metamorphosed calcareous sedimentary rocks. Bismuthinite is somewhat restricted in its occurrence to those deposits that are closely related to igneous rocks. It is associated with cassiterite, magnetite, sphalerite, galena, chalcopyrite and pyrite.

In general, there are three classes of bismuth deposits: (1) Bismuth-tin deposits, in which the bismuth minerals are associated with tin, copper, tungsten and molybdenum minerals (the Bolivian, Korean, Canadian and Chilean deposits, and those in Peru), (2) The bismuth-cobalt deposits, in which the bismuth minerals are associated with cobalt and uranium (the Saxony deposits), and (3) The bismuth-gold deposits, in which bismuth minerals are closely associated with the gold in gold-quartz veins (deposits in the United States, New South Wales, Queensland and Norway).

Virtually all bismuth is obtained commercially from two sources: (1) as a by-product from the smelting and refining of lead and other base-metal ores and concentrates, and (2) from ores treated chiefly for their bismuth content and for one or two associated metals, such as tungsten and tin. A large part of the domestic supply is obtained as a by-product of the smelting and treatment of domestic and foreign lead bullion and non-ferrous ores of lead, silver, copper and gold. The principal domestic sources are the lead-silver, lead, copper and zinc ores of the Bisbee, Pima and Big Bug districts in Arizona; the Upper San Miguel, Leadville, Rico and Creede districts in Colorado; the Coeur d'Alene, Warm Springs and Alder Creek districts in Idaho; the Butte district in Montana, and the Park City, Tintic and West Mountain districts in Utah.

The principal foreign sources of bismuth are the copper, lead and silver deposits of Peru (from mines operated by the Cerro de Pasco Corporation), the lead de-

posits of Mexico, the tin deposits of Bolivia, and a large tungsten mine in the province of Kangwon, southern Korea (Renick, 1956, p. 2).

**Localities in California.** Most of the occurrences of bismuth-bearing minerals in California are associated with ores of copper, lead, silver and tungsten. Oxidized bismuth minerals occur with garnet, epidote, clinozoisite, and other contact metamorphic minerals in a highly metamorphosed limestone at the United Tungsten copper mine in the Moronga district, San Bernardino County (Hess and Larsen, 1922, p. 261). Native bismuth and several oxidized bismuth minerals have been reported with arsenopyrite and gold in quartz veins at the Big Blue group of mines, Kern County (Prout, 1940, p. 413).

In 1909, twenty tons of bismuth ore were mined at the Lost Horse, formerly the Lang copper mine, in the Piñon Mountain district, Riverside County. The bismuth occurs in the form of a bismuth sulfide associated with copper minerals in a quartz vein that cuts a pre-Cambrian (?) foliated, micaceous quartzite. The vein ranges in width from a few inches to 5 feet and has been prospected along a strike length of at least 800 feet. The workings consist of an 80-foot tunnel, a winze 50 feet deep, and a 50-foot drift extending east from the bottom of the winze. The mine has been worked chiefly as a gold property (Tucker and Sampson, 1929, p. 483).

Native bismuth, bismuthinite and bismutite occur with tourmaline, lepidolite and other pegmatite minerals at the gem mines in Pala (Kunz, 1903, pp. 398-399), Rincon (Rogers, 1910, p. 208), and Jacumba (Sanford and Stone, 1914, p. 25). At the Garnet Dike tungsten mine in Fresno County, concentrates containing up to 14 percent bismuth were obtained. The ore mineral is bismuthinite and occurs with scheelite in a tactite zone having the form of a vertical chimney, with a maximum diameter of about 60 feet (Logan, Braun and Vernon, 1951, p. 532).

No attempt was made to recover the bismuth from the tungsten concentrates. Moreover, insufficient ore remains in the mine to encourage mining for bismuth.

Deposits where bismuth minerals occur in trace amounts, varying from a few hundredths of 1 percent to a percent or so, do not constitute commercial reserves of bismuth principally because of the low grade of the deposits and the general lack of recoverable valuable metals or minerals.

**Recovery.** The domestic lead, zinc and copper ores that contain bismuth are concentrated by selective flotation. At the smelter, the copper-rich concentrates are roasted to eliminate sulfur, and most of the lead and bismuth remain in the calcine. The calcine is then smelted to a copper matte which collects most of the bismuth and lead. During the converter treatment of the copper matte to blister copper, most of the lead and bismuth is fumed off and a small part carried away by the converter slag. Copper smelters are equipped with baghouses or Cottrell precipitators to collect the fumes and dust.





FIGURE 1. Map showing mines where bismuth has been found in California. 1, Garnet Dike mine area, Fresno County; 2, United Tungsten Copper mine area, San Bernardino County; 3, Lost Horse mine, Piñon mining district, Riverside County.

The bismuth in lead concentrates and lead ores is collected in the lead bullion during the lead-smelting. If the bismuth is present in excessive amounts in the lead bullion, it is considered a detrimental impurity and must be removed before the lead can be used. Several processes for removing the bismuth from lead bullion are in use, and the most widely used processes are: (1) crystallization, (2) electrolytic refining (Betts), and (3) the Betterton-Kroll process. Electrolytic refining processes employing chloride electrolyte and fluosilicate electrolyte have been used, and have not been able to compete successfully with the pyrometallurgical process which produces pure bismuth much cheaper (Renick, 1956, p 5).

**Utilization.** Bismuth has many properties which make it useful in many fields. It melts at  $271^{\circ}\text{C}$ , and expands 3.32 times during solidification. Bismuth has a low thermal conductivity of 0.018 calorie per second per cubic centimeter at  $100^{\circ}\text{C}$ , lower than for any other metal except mercury. Its coefficient of expansion at  $0^{\circ}$  to  $100^{\circ}\text{C}$ , is 0.00000731. Bismuth has a surface tension

lower than that of any of the metals with which it is alloyed, such as tin, lead, antimony, and cadmium.

The principal use of bismuth in the United States is in the manufacture of alloys, mainly solder, fusible alloys, and special alloys, all of which, in 1953, consumed 1,026,000 pounds of bismuth metal or 65 percent of the national consumption. Some of the special alloys, such as the "eutectic" and "noneutectic" alloys, have low melting temperatures, lower than that of pure bismuth metal. Melting temperatures for some eutectic alloys (alloys containing varying proportions of Bi, Pb, Sn, Cd, Zn, Sb, and In) range from  $117^{\circ}$  to  $390^{\circ}\text{F}$ . Melting temperatures for some of the noneutectic alloys (alloys of the same listed metals) range from  $64^{\circ}$  to  $271^{\circ}\text{F}$ . (Encyclopedia of Chemical Technology, 1948, pp. 626-534). Some of the bismuth alloys are used in the making of precision castings. The addition of a small amount of bismuth to alloys containing lead and tin helps reduce the surface tension in the alloy and thereby producing sharply defined casting even when the percentage of bismuth is insufficient to cause the alloy to expand and





FIGURE 2. Crystals of bismuth metal made by remelting bismuth in the furnaces of the American Smelting and Refining Company at Omaha, Nebraska. Photo by Mary Hill.

fill the mold upon solidification. Also, the addition of very small amounts of bismuth (0.1 to 0.2 percent of the weight of the casting) to either molten gray or white iron produces greater fluidity of the hot alloy and hence form cleaner, sharper castings. These low melting point alloys are used in the manufacture of safety devices (overhead sprinkling systems in factories, warehouses, and department stores). The Cerro de Pasco Corporation has developed a number of bismuth alloys and the following are several of these alloys and some of their uses: Cerromatrix—used for anchoring sheetmetal punches and dies, bushing in drill fixtures, and bushing and non-moving parts in machinery; Cerrobases—used in preparing master patterns for foundry match plates, and glass-to-metal hermetic seal; and Cerrobend—used as filler to support tubing during bending to prevent wrinkles, and as a heat transfer medium (Renick, 1956, p. 7).

Several new uses have been developed for bismuth alloys. One of these is in the development of nuclear power as solutions of liquid metals containing uranium, thorium, bismuth, and tin have been found to be useful in reactor designs (Teitel, et al., 1954, pp 14-15). A new metallic "permanent magnet" alloy of bismuth and manganese has been found to have the highest coercive force of any known substance and also high resistance to demagnetization. This alloy is formed as a powder and can be molded into many different shapes (U. S. Naval Ordnance Laboratory, 1952, pp. 1-15).

Bismuth also is used in the manufacture of bismuth compounds which are widely used in medical and cosmetic preparations. This use, in 1953, consumed 414,000 pounds of bismuth metal, or 27 percent of the national consumption. Bismuth subcarbonate and nitrate are opaque to X-ray and are taken internally before X-ray photographs are made of the digestive organs. Bismuth subnitrate, bismuth subgallate, and bismuth subsalicy-

late are used extensively in cosmetic preparations, soothing intestinal disorders, and the treatment of venereal diseases (Condensed Chemical Dictionary, 1942). In addition, some organo-metallic compounds of bismuth have "anti-knock" properties, but are only about one-third as efficient as lead compounds in this respect (Renick, 1953, p. 7).

**Marketing.** The principal smelters where refinery bismuth is produced are American Smelting and Refining Company, Omaha, Nebraska and Perth Amboy, New Jersey; the United States Smelting and Refining Company, East Chicago, Illinois; and the Anaconda Copper Mining Company, Anaconda, Montana. The Cerro de Pasco Company, Peru, is the principal foreign source of bismuth, as well as the principal consumer and importer of bismuth metal.

Most of the bismuth alloys used in California are prepared by the smelters where the bismuth is recovered as a by-product in the smelting and refining of lead-silver and base-metal ores and concentrates. The bismuth chemicals, likewise, are shipped into California from manufacturing firms in the east.

In 1957, the New York market quotation on refined bismuth metal in ton lots was \$2.25 per pound (E & M J Metal and Mineral Markets). Bismuth used in the pharmaceutical and medicinal trades must be absolutely free from arsenic and have a purity of 99.99 percent (Renick, 1953, p. 9).

Bismuth-bearing concentrates are penalized for the bismuth on the basis of \$0.50 per pound of the metal. Any concentrate containing as much as one percent bismuth in the mineral form would be considered a high-grade concentrate. Such concentrates are readily accepted by the smelters whose concentrates usually contain around 0.1 percent bismuth.

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## BLACK SANDS \*

BY MELVIN C. STINSON

Black sands in California have been of interest to miners and prospectors since the discovery of gold more than 100 years ago. Although for many years gold and minor amounts of platinum and amalgams (native alloys of mercury with gold and silver) have been recovered from placer stream sands in California, no other heavy constituents have been recovered on a continuing basis from such deposits. The possibility of extracting such other heavy materials as magnetite, ilmenite, chromite, zircon and garnet, however, has attracted the attention of numerous persons, and, from time to time, the commercial recovery of magnetite, ilmenite, chromite, and zircon has been attempted. These operations have generally proved short-lived because of the small reserves of raw material in the areas tested and a lack of west coast market for the heavy minerals. Monazite, a heavy mineral which is locally abundant in black sands, is of interest in California as a potential source of rare earths and thorium.

Although most of these heavy minerals, or the elements that they contain, are discussed elsewhere in this volume, they are considered collectively here because the black sand that they comprise is, in a broad sense, a single mineral commodity which can be mined as such and then separated into useful components.

*Mineralogy and Geologic Occurrences.* "Black sands" is a term commonly applied to alluvial deposits containing appreciable quantities of heavy, dark-colored iron-bearing minerals. In general, black sands consist of hard minerals ranging in specific gravity from 3 to 7, mingled with small percentages of metals and metallic minerals with specific gravities between 7 and 20. Day and Richards (1906, p. 1175), in an early study of black sands in the placer mining regions of California, noted that the following minerals occur most frequently in placer sands: magnetite, gold, ilmenite, garnet, zircon, hematite, chromite, platinum, iridosmine, mercury, amalgam, olivine, iron silicates, pyrite, monazite, copper, cinnabar, cassiterite, and corundum.

Resistance to chemical and mechanical weathering and a high specific gravity cause such minerals to be concentrated in black sand. The preponderance of magnetite and ilmenite in these heavy sands causes the black color. The nature of the assemblage of heavy minerals in a given black sand is determined by the character of the source rocks.

The source rocks, from which the common heavy minerals are derived, are shown below:

<i>Mineral</i>	<i>Most common source rock</i>
Magnetite	Very common in small amounts in most rocks. Occurs in abundance in some metamorphic rocks, and some basic igneous rocks. Magnetite is usually the most abundant mineral in black sands.
Ilmenite	Common in small amounts in most rocks, often with magnetite. Abundant in such rocks as gabbro, anorthosite, and diorite. Locally present in pegmatites and massive quartz veins.

<i>Mineral</i>	<i>Most common source rock</i>
Gold	Quartz veins in crystalline rocks. Most of the gold-bearing quartz veins in California are associated with late Jurassic plutonic rocks of the Sierra Nevada and Klamath Mountains.
Garnet	Common in crystalline rocks. Most common in mica, hornblende, and chlorite schists, and in gneiss; in crystalline limestones and in contact zones; also in granite and syenite.
Zircon	Widespread in small proportions in acidic intrusive rocks; most abundant in granite, syenite, diorite, and pegmatites.
Hematite	Very widely distributed in many rock types. Most abundant in igneous and metamorphic rocks.
Chromite; platinum group	Chiefly in basic and ultrabasic rocks, including peridotites and derived serpentine.
Mercury; amalgam	In the gold placer sands because of mining operations and processes.
Olivine; iron silicates	Common in basic and ultrabasic igneous rocks and some metamorphic rocks.
Pyrite; chalcopyrite	Most common in association with metallic ore deposits. Locally abundant in metamorphic rocks.
Monazite	An accessory mineral in granites, gneisses, aplites, and pegmatites.

Black sand occurs in all water-borne sands and gravels. When first broken free from their parent rocks, the heavy minerals form but a small percentage of the alluvial material, rarely exceeding 2 percent. They are concentrated by streams, ocean waves, and occasionally by wind, to form sands that locally consist almost wholly of heavy minerals.

Beach deposits of black sands are formed initially, between low and high tide levels, by the concentrating action of the surf waves which is most effective during storms. Most of the individual bodies of black sand in beach deposits tend to be lenticular in cross-section and to be distributed erratically. They are characterized by a pinching and swelling, both vertically and laterally, which are controlled largely by the irregularities of the bedrock near the shoreline upon which the heavy-mineral deposits are formed. The internal structure of a deposit ordinarily consists of many discontinuous layers and lenses containing quartz and heavy mineral grains in various proportions; some layers consist of almost pure quartz sand, whereas other consist almost entirely of heavy minerals. The layers and lenses range in thickness from a fraction of an inch to a foot or more. Cross-bedding and truncated layers are common.

Large amounts of black sand have been artificially concentrated in the hydraulic tailings, dredge tailings, placer clean-up sands, and dredge clean-up sands in the gold placer districts in California.

No extensive study of the distribution and relative abundance of heavy minerals in placer and beach sand deposits has been made in California since 1905 when Day and Richards (1906, pp. 1175-1258) investigated the heavy sands in waste thrown out of the sluice boxes in the clean-up of placer mines. Some of the beaches along the coast were also sampled and the heavy minerals

\* In part extracted from section by G. B. Oakeshott in California Div. Mines Bull. 156, 1950.



Table 1. Number of localities having concentrations of the listed heavy minerals.

Mineral	Over 1000 lbs. per ton of black sand	From 500 to 1000 lbs. per ton of black sand	From 100 to 500 lbs. per ton of black sand
Magnetite.....	56	35	36
Ilmenite.....	7	19	50
Chromite.....	4	6	44
Hematite.....	2	7	23
Garnet.....	2	3	13

studied. The results of this study appeared as a table showing the concentration of each heavy mineral in pounds per ton of black sand. Table 1 is a summary showing the relative abundance of the commoner heavy minerals at 182 localities in California.

In general, the concentration of magnetite was found to be the highest and most widespread of the heavy minerals. Notable high concentrations of ilmenite and hematite were found in some of the counties in the Mother Lode region and along the coast. High chromite concentrations were found in beach deposits along the northern coast and in placer deposits in western Butte, Plumas, Placer and Sacramento Counties. High concentrations of garnet occur in beach deposits near Fort Bragg in Mendocino County and Point Sal in Santa Barbara County. Many other localities are given and the interested reader should refer to the original article.

In summary, streams that drain areas of acidie igneous rocks generally concentrate magnetite, ilmenite, garnet zircon, and locally monazite. Chromite, magnetite, and ilmenite are most common in sands of streams that drain areas of basic or ultrabasic igneous rocks.

*Methods of Treatment.* In recent years most of the world's supply of heavy minerals has been obtained from Australia and Florida beach sand deposits and intermittently from placer deposits in Idaho. The methods of treatment of the Australian beach sands is given in the section on zircon in this volume.

The beach deposits near Starke, Florida are largely silica and contain about 1.3 percent titanium oxide (Eng. & Min. Jour., May 1952, p. 85). The sand is mined with a dredge which pumps sand and water to a wet plant mounted on barges. The wet plant consists of the conditioner barge, rougher barge, and a cleaner barge.

On the conditioner barge is the washing and thickening equipment, including screens and rake classifiers. The rougher barge carries the first-stage separation equipment. The cleaner barge carries the last two stages of the work of preparing the concentrate before delivery to the final washer. The three wet plants contain a total of 1100 Humphreys spirals. Concentrates from the wet mill average about 27 percent titanium oxide. Of this concentrate, 80 percent is heavy minerals consisting of 45 percent titanium minerals and 15 percent zircon. The remaining 40 percent of the heavy minerals have no present commercial value. The concentrate from the wet plant is dried and fed by a screw conveyor for distribution to 28 rougher high-tension (40,000 volts) electrostatic separators. The concentrate from these separators are sent to a magnetic separator for further investigation. The tailings from the electrostatic separators

and magnetic separators are sent to the zircon concentrating plant for further concentration.

In the Cascade Basin of Idaho, placer sands have been mined by electrically powered dredges which handle from 4,000 to 6,000 cubic yards of gravel per day (24 hours) (Min. Cong. Jour., March 1954, p. 33). Endless chains of buckets bring the material to the surface from a maximum depth of 70 feet and the loads are dumped at the rate of 24 buckets per minute. The heavy minerals are separated from the gravel and earth within the dredge by screening and jigging. From the dredge, the heavy sand is trucked to a separating plant. The dried sand is placed on a belt and run through a series of magnets of varying degrees of intensity to separate the ilmenite, garnet, monazite, and zircon. From every 4,000 tons of gravel dredged, about 30 tons of heavy sand concentrates are recovered. This 30 tons yields approximately two tons of monazite, from 20 to 25 tons of ilmenite, and the balance in zircon, garnet, and silica (see sections on abrasive materials, rare earths, thorium, and zirconium-hafnium in this volume).

*Production and Utilization.* To date, gold and the platinum group metals have been the chief minerals recovered from the black sands of California (see sections on gold and platinum in this volume). In black sands these minerals generally occur in fine flakes and scales, and much of the gold in former-beach deposits is tarnished. The tarnish, or "rust" as the miners call it, makes the gold difficult to save in the sluice box and on the amalgamation plates. The impression that gold and platinum in black sand exists in some peculiar form and that they cannot be recovered by any known means is fairly widespread. That gold in black sand concentrations is entirely amenable to cyanidation and chlorination, however, has been well demonstrated. Satisfactory amalgamation of the "rusty" gold usually can be accomplished by grinding the material to scour and brighten it so that it will be taken up on contact with mercury.

Black sands near Aptos, Santa Cruz County, and Redondo Beach and Sand Canyon in Los Angeles County, have been marketed because they contain a high percentage of ilmenite and magnetite (see section on titanium in this volume). For many years the black beach sands at Aptos have been utilized intermittently by several companies (Laizure, p. 82-84). Of these, the principal consumer was the Triumph Steel Company which produced sponge iron, briquetted magnetite, alloy steel, and ferrotitanium, but was apparently unable to show a profit in its operation. The owners of the Live Oaks mine in Sand Canyon, Los Angeles County, operated an electromagnetic mill intermittently from 1944-1948 to produce ilmenite and magnetite used for roofing granules, pigment, and heavy aggregate.

In 1926, two experimental plants at Hermosa Beach (Gay and Hoffman, 1953, p. 641) were using titaniferous sands from the beach between Redondo Beach and Palos Verdes. In 1955, one plant was producing granules for roofing paper from black sands from this locality (Gay, personal communication).

During World War II a private operator attempted to recover chromium from magnetite-chromite sands in Clear Creek not far from Hernandez, San Benito



County. The operation was unsuccessful because the operator could not develop suitable reserves of chromite-rich sand.

The recent interest in black sands (exclusive of precious metals) has centered largely about the possible recovery of ilmenite, rutile, zircon, and monazite. Most of the production of these minerals from black sands in the United States is from the previously mentioned dunes near South Jacksonville, Florida, and from placer deposits in the Cascade Basin, Idaho.

The first production of commercial zircon in California was reported in 1937. This was from a dragline dredge near Lincoln, Placer County. The zircon was used in sandblasting and for experimenting in the manufacture of refractories. A small amount of zircon was also shipped from Lincoln in 1941 for use in steel alloys.

No known concentrations of monazite sands of present commercial importance exist in California, although sands near Crescent City have been found to contain as much as 56 pounds of monazite per ton of sand concentrate; and sands near Nevada City contained as much as 4 pounds per ton of concentrate (Day and Richards, 1906, p. 1185).

Uranium minerals occur in small quantities in some alluvial deposits, but no commercial amounts have been discovered. Uranoan thorite in sands along the beach between Half Moon Bay and Monterey was discovered only recently (Hutton, C. O., 1952, pp. 80-90). A ton of sand along these beaches will yield one pound of uranoan thorite which contains 7 percent uranium oxide. This concentration is considered to be too low for profitable extraction at the present time.

**Markets.** In California, no market exists for black sands as such but concentrates of several of the heavy minerals can be sold.

There is only a limited market for magnetite or hematite sands in California because most of the large iron smelting companies use iron ore from their own mines. A small amount of magnetite or hematite sand could probably be sold for iron ore provided that it was sintered to reduce the dust loss in shipping and in charging the furnaces. The sintered material might also be sold for export to Japan provided a sufficient reserve of magnetite-hematite sand could be developed. Limited quantities of magnetite or hematite sand are used in heavy aggregate and as ballast.

Chrome-free ilmenite containing 59.5 percent titanium oxide may be sold on the east coast as titanium ore if it could be cheaply mined and concentrated. There is no present market for ilmenite as titanium ore on the west coast.

Chromite (titanium-free) containing more than 42 percent chromic oxide and a minimum of 2 to 1 chromium to iron ratio may be sold to the General Services Administration for government stockpile.

Garnet sand may be used for the abrasive coating of papers and cloths if the required grain size, purity, and content of fine material can be controlled. The garnet should be capable of being broken into fragments about  $\frac{3}{16}$  inch in diameter; should contain no impurities, and a minimum of fine material. Most garnet sand from placer deposits is much too fine-grained to satisfy these conditions. A limited amount of garnet sand is used for sandblasting by the aircraft industries.

Most of the heavy minerals found in black sands could probably be sold provided that a steady source of relatively pure material could be produced cheaply from an extensive deposit.

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## BORON

BY WILLIAM E. VER PLANCK

The world's largest known reserves of boron minerals are in southeastern California. In recent years these deposits have supplied not only the needs of the United States but over nine-tenths of the world's requirements. Elemental boron has limited uses, but borax and boric acid are exceeded by few chemicals in the extent of their application.

At present borax and kernite together with borate brines are the most important sources of boron and its compounds in California. The state also contains deposits of colemanite and low grade playa deposits consisting of borax and ulexite that have been worked on a large scale in the past. Small quantities of colemanite are currently being mined for special uses, but the playa deposits have been idle for nearly 50 years. Ulexite is the boron mineral mined in Chile and Argentina, whereas priceite is mined in Turkey, sassolite in Italy, and boracite in Germany.

**Mineralogy.** Of the many minerals containing boron, by far the most important commercially are the borates. The sodium borates form a series the members of which are characterized by different amounts of water of hydration. Borax ( $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ ) forms milky white translucent to opaque crystals many of which are large. It is readily soluble in water. On exposure to dry air borax dehydrates to tincalconite ( $\text{Na}_2\text{B}_4\text{O}_7 \cdot 5\text{H}_2\text{O}$ ), a finely crystalline, dull, white powder. Kernite ( $\text{Na}_2\text{B}_4\text{O}_7 \cdot 4\text{H}_2\text{O}$ ) commonly forms in masses of prismatic crystals which, when pure, are glassy clear. Three well-developed cleavages cause it to break into characteristic splintery fragments. Kernite also will hydrate to tincalconite.

The calcium borates form a series which includes inyoite ( $\text{Ca}_2\text{B}_6\text{O}_{11} \cdot 13\text{H}_2\text{O}$ ), meyerhofferite ( $\text{Ca}_2\text{B}_6\text{O}_{11} \cdot 7\text{H}_2\text{O}$ ), colemanite ( $\text{Ca}_2\text{B}_6\text{O}_{11} \cdot 5\text{H}_2\text{O}$ ), and priceite ( $\text{Ca}_5\text{B}_{12}\text{O}_{23} \cdot 9\text{H}_2\text{O}$ ). Colemanite occurs in white to gray prismatic crystals or granular masses. It is transparent to translucent and is but slightly soluble in water.

The sodium-calcium borates include ulexite ( $\text{NaCaB}_5\text{O}_9 \cdot 8\text{H}_2\text{O}$ ) and probertite ( $\text{NaCaB}_5\text{O}_9 \cdot 5\text{H}_2\text{O}$ ). Ulexite forms rounded masses, called cottonballs, made up of loosely knit, fine, acicular crystals. Less commonly it occurs as a dense, cross-fibered vein filling cutting other borates. Probertite forms radiating, needle-like crystals associated with ulexite.

Other boron minerals of commercial interest are sassolite or natural boric acid ( $\text{H}_3\text{BO}_3$ ) and boracite ( $\text{Mg}_6\text{Cl}_2\text{B}_{14}\text{O}_{26}$ ). Howlite ( $\text{H}_5\text{Ca}_2\text{B}_5\text{SiO}_{14}$ ) is associated with colemanite but is not of commercial interest because of its silica content. Tourmaline and other complex borosilicates are found in igneous rocks.

**Geologic Occurrence.** Boron is believed to be a constituent of magmas. Not only do igneous rocks contain borosilicates, but boric acid is present in hot springs and is deposited near solfataras. Boron has been detected in sea water, and the boracite present in the Stassfurt deposits is thought to have been derived from evaporated sea water. Some saline lakes, particularly those in regions of recent volcanic activity, have a high borate content; examples of these in California include Searles

Lake, Owens Lake, and Borax Lake (see general discussion of salines in this volume). The brine of Searles Lake supplies a significant part of the borax produced in California.

Certain playas contain borates in the efflorescent crusts that form during dry weather. In California, borate-bearing crusts have been worked in Searles Lake, Death Valley, Amargosa Valley, Koehn Lake, Salt Wells Valley, and Saline Valley. Many borate crusts consist of borax, cottonball ulexite, and tincalconite mixed with various proportions of other saline minerals, but calcium borates do not occur in Searles Lake. The borate crust from Searles Lake averaged slightly more than  $7\frac{1}{2}$  percent borax (Hanks, 1883, pp. 26, 27). The crusts are only a few inches thick, but they may form again when removed.

The borates of saline lakes and playas are thought to have been derived in part from hot springs and in part from material leached from older borate deposits. Some such explanation is necessary to account for the concentration of borate in these deposits.

Deposits of colemanite have been mined in California in the Furnace Creek area of Death Valley and near Shoshone, Inyo County; in the Calico Mountains near Daggett, San Bernardino County; near Lang in Los Angeles County; and in the northeastern corner of Ventura County. In Nevada, a large deposit of colemanite exists in the Muddy Mountains, Clark County. Although colemanite is the principal borate mineral, other calcium borates, sodium-calcium borates, and howlite usually are present. The borate minerals are associated with folded Tertiary lake beds, tuffs, and basalt flows. In some of the deposits limestone is present.

Although in a few deposits the borates form uniform beds parallel to the enclosing sediments, they generally occur as highly irregular, lenticular masses that cut across the bedding. Typically, the borates are confined to a particular group of beds within which they swell to form comparatively large masses and pinch to a thin layer of scattered nodules. These bodies consist of colemanite in cleavable, crystalline masses or exhibiting radiating structures. Openings lined with clear crystals are often present in massive colemanite, and some deposits consist largely of hollow, crystal-lined nodules of colemanite. Colemanite also forms comparatively thin columnar or cross-fibered layers in shale. Most deposits contain howlite in the form of nodules in the colemanite and associated shale or of seams in the shale. A compact variety of ulexite is usually present and locally is the principal borate. Minor amounts of inyoite, meyerhofferite, and probertite are not uncommon.

The Death Valley colemanite deposits are the largest in California. In the Furnace Creek area the deposits occur in the Furnace Creek formation of probable late Miocene to Pliocene age which is exposed in a northwest-trending topographic and structural trough that separates the Black Mountains on the southwest from the Funeral and Greenwater Ranges on the northeast. The principal structure is a syncline along the front of the Funeral Mountains. The Furnace Creek formation (No-



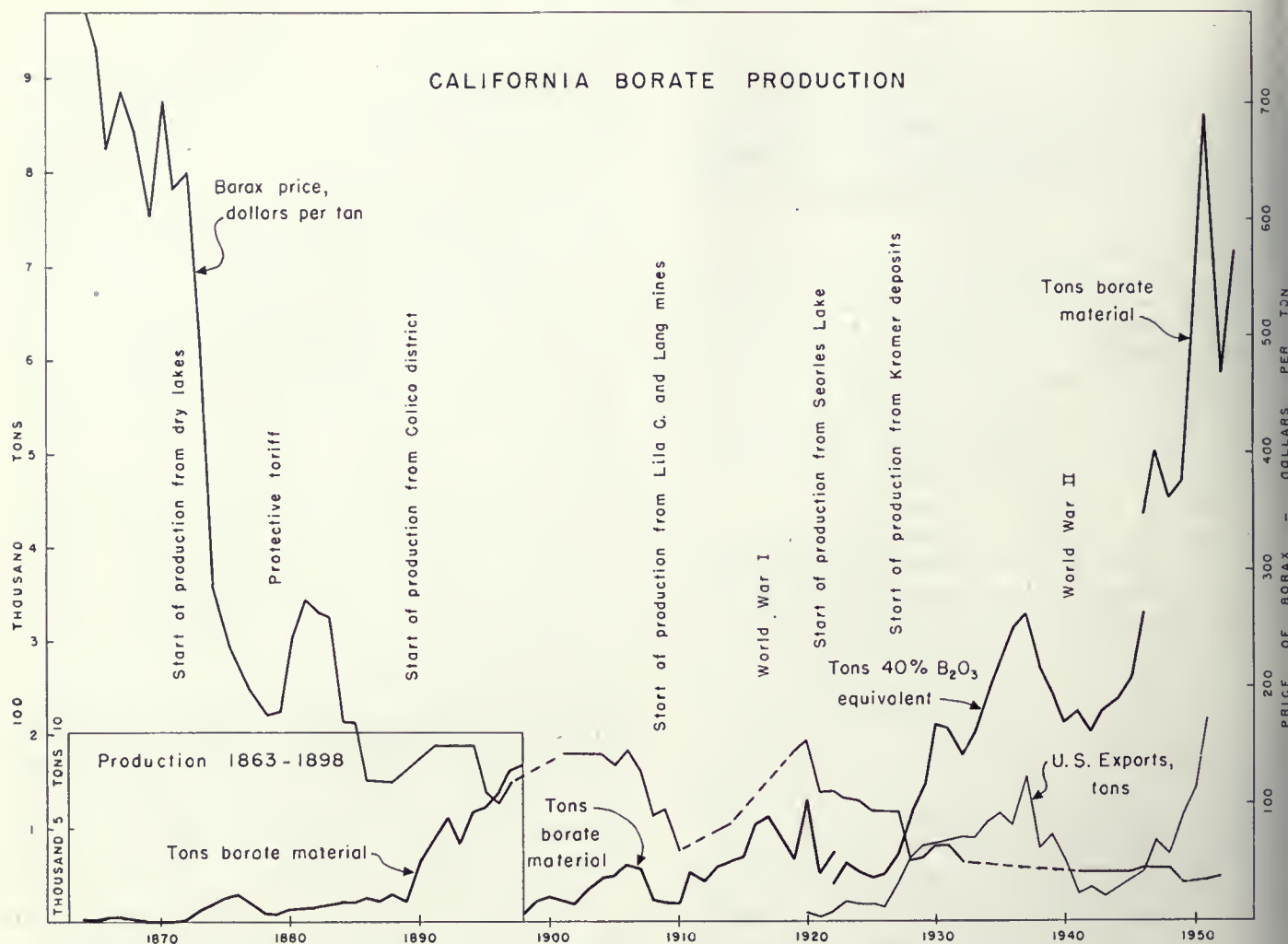


FIGURE 1. Chart showing production of borates in California, price of borax, and exports of borates from the United States.

ble, L. F., 1941) shows marked lateral transitions in lithology. It consists of folded lava flows, tuff, and breccia with interbedded fanglomerate, yellowish sandstone, and tuffaceous clay shale. The colemanite deposits are in playa sediments that interfinger with the volcanic rocks and that are discontinuously exposed along a northwest-trending belt about 20 miles long. The principal workings are at Ryan, but colemanite also has been worked in Gower Gulch, Twenty Mule Team Canyon, and Corkscrew Canyon.

In the vicinity of Ryan, borate-rich beds occur in thin bedded, light colored shales beneath basalt flows of the Funeral fanglomerate that unconformably overlie the Furnace Creek formation. Just beneath the basalt cap are masses of colemanite and other borate minerals from a few inches to a maximum of 70 feet thick that have been mined. Some of the ore was shipped without treatment, but much of it was beneficiated to remove interbedded shale. Lower in the formation are borate-bearing clays that rest upon thick beds of coarse sandstone and tuff.

Several theories have sought to explain the origin of the colemanite deposits, but it is now generally believed that they are Tertiary playa deposits that have been

elevated and folded. Drainage having been thus provided, the sodium borate was leached from the original ulexite leaving the insoluble calcium borate, colemanite (Foshag, F. W., 1921).

Playa borate deposits are known in all the deserts of the world, and colemanite beds of the type described occur in Nevada as well as in California; but the thick beds of crystalline borax and kernite near Kramer are unique. These deposits, described by Gale (1946), lie in a basin containing Tertiary rocks of the middle Miocene Rosamond and upper Miocene Ricardo formations.

The Ricardo formation in the Kramer area is divisible into three distinct units which from bottom to top are (1) the Saddleback basalt flows, (2) the borate-bearing lake beds, and (3) the post-borate conglomerate. The lake beds are in turn composed of three recognizable parts. The lowermost 30 to 50 feet is known as the foot-wall shale, a dark greenish to black slate containing seams or veinlets of ulexite and howlite. This unit, where present, directly overlies the basalt flows. The principal borate deposits are contained in the blue shale, or middle lake bed unit, which is 200 to 250 feet thick and is characteristically clayey and thinly laminated. The uppermost lake bed unit is the green shale, 30 to 50



et of green, thinly bedded, micaceous shales that contains no borates.

Nodular masses of colemanite and ulexite are widely, though irregularly, distributed in the blue shale unit throughout the Kramer area; but the sodium borate nodules, which are of much greater commercial importance, underlie a  $1\frac{1}{2}$ - by  $\frac{1}{2}$ -mile area in the center of the basin. These are characteristically tabular beds or layers of borax and kernite with a minor amount of interbedded shale commonly as much as 250 feet thick. The borate beds are preserved in a synclinal structure that has been modified by subsidiary folding and minor faulting. The borate deposits now lie at depths of from 150 to 1,000 feet beneath the surface.

The Kramer borates, Gale (1946) believes, were derived from volcanic gases or water that issued during and immediately after the extrusion of the Saddleback basalt. Relatively pure borax was precipitated by the boiling of the hot, saturated solution of mixed salts that accumulated in the basin. The borax was later covered by clays and in part altered to kernite. The presence of small amounts of realgar and stibnite suggests that the alteration may have been caused by heat. Ripple marks in the sediments interbedded with borax, and an egg shell found in it, suggests that borates formed in shallow water.

*Localities and History of Production in California.* Two sources, the Kramer deposit and Searles Lake, now contribute nearly all of the borates produced in California. A comparatively small amount of colemanite is produced near Shoshone and in Corkscrew Canyon, Inyo County, and a little borax is recovered from the brine of Owens Lake. At various times all the other types of deposits have been important borate sources, but each has become noncommercial with the successive discovery of larger and richer deposits. The history of the industry in the western United States can thus be divided into four periods. The first began in 1864 with the discovery of borax in Borax Lake and Hachinhama Lake, Lake County, California. Borax crystals were recovered from the mud of these lakes and from lake water which was evaporated in small pans.

The second period began in 1872 when the recovery of ulexite and borax from playa surfaces in Nevada put an end to the Lake County operation. A crustal operation at Searles Lake began in 1874, but for some 10 years the Nevada production exceeded that from California. The crusts at Death Valley and Amargosa Valley were worked for a comparatively short time beginning in 1882 or 1883. Borax was also recovered from Koehn Lake, Salt Wells Valley, and Saline Valley. The laborious process of scraping up and refining the borate material has been described by Hanks (1883).



FIGURE 2. Photograph of a 20-mule team used to haul borax from Death Valley to Mojave, 1883-90. Photo by Ann Rosener.



The Death Valley crustal operations terminated about 1890 when the colemanite beds in the Calico Mountains near Daggett were first worked. The playa operations continued on a decreasing scale for a number of years. The last playa production of borates in California appears to have been from Saline Valley in 1907. Also in 1907, colemanite mining began in Inyo County, and at about the same time the Los Angeles and Ventura County colemanite deposits were developed. At Searles Lake production of borax from the brine began in 1919 and from Owens Lake in 1929.

The fourth and present period began in 1927 when the large scale production of sodium borates from the Kramer deposit made the colemanite deposits of less economic interest. Borates in the Kramer district were discovered accidentally in 1912 or 1913 by Dr. J. K. Suckow who was drilling a water well. It was not until 1925, however, that the sodium borates were noted in a drill hole, and another year passed before the deposit was reached by a shaft sunk by the Pacific Coast Borax Company. A new sodium borate was recognized, and its analysis was reported by the laboratory of the Pacific Coast Borax Company at Wilmington, California, on August 18, 1926. The new mineral was named *rasorite* after Clarence R. Rasor, field engineer of the United States Borax Company.

In the meantime W. T. Schaller obtained some samples of the new mineral and determined its properties. Not knowing that the borax company was already using the name *rasorite*, Dr. Schaller called the new mineral *kernite*, the name most used today.

**Operations.** In 1955, three companies accounted for practically all of the borates produced in California. Sodium borate minerals were mined by Pacific Coast Borax Co., Division of Borax Consolidated Limited near Boron in the Kramer district, while borax was among the products produced from the brine of Searles Lake by the American Potash & Chemical Corporation and the West End Chemical Company. During the year a fourth company, the California Borate Company, obtained title to some borate land in the Kramer district and in 1956 was preparing to mine sodium borates. The Pittsburgh Plate Glass Company, Columbia Chemical Division, has produced borax as a by-product of soda ash recovery from the brine of Owens Lake, but since World War II the production of borax has been small. In addition, Pacific Coast Borax Co. and its affiliate, United States Borax Company, produce a small amount of colemanite from mines near Shoshone and Ryan.

At present Pacific Coast Borax Co. works its sodium borate deposit near Boron with three separate mines: the Baker and West Baker mines, developed in 1926, and the Jenifer mine, developed in 1950 and 1951. All three mines have been opened with vertical shafts and a system of drifts and crosscuts that totals several miles. In the older mines the ore is mined either by open stoping or shrinkage stoping. The ore is broken by drilling and blasting, loaded into cars, and trammed to the shaft stations in the conventional manner. The stopes are about 20 feet wide, more than 100 feet long, and up to 100 feet high. In addition to ore left in pillars between the stopes, some ore is left on the foot wall and hanging wall for support of the weak shale. To provide additional



FIGURE 3. Photograph showing removal of overburden in preparation for open-pit mining at Boron. Photo by Ann Rosener.

support, the completed stopes are filled with gravel introduced through a bore hole from the surface (Tucker and others; 1949, pp. 243, 244). In the Jenifer mine the ore is removed with continuous mining machines without the use of drilling and blasting, and the broken ore is taken to the shaft station with a belt conveyor system (Pacific Coast Borax Co., 1951, p. 51).

Ore from the three mines is brought to a central plant where it is crushed, screened and passed through magnetic separators that remove a portion of the shale impurities (Pacific Coast Borax Co., 1951, pp. 51, 52). Some of the magnetic concentrates are sold as Fertilizer Borate and Borasen. Most of the magnetic concentrates are dehydrated to various degrees to produce Rasorite Special Concentrates, Fertilizer Borate High Grade, Anhydrous Rasorite, and Concentrated Borasen. The dust unavoidably produced in the plant is collected and made into borax in a small plant at Boron.

Some of the crude ore is shipped to Pacific Coast Borax Co.'s refinery at Wilmington, Los Angeles County. Here, after crushing and screening, it is dissolved; and all insoluble matter is removed (Connell, 1950). The clear borate solution is then sent to the granulators where, by controlling the temperature and concentration, both borax ( $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ ) and sodium borate pentahydrate ( $\text{Na}_2\text{B}_4\text{O}_7 \cdot 5\text{H}_2\text{O}$ ) are produced. These products are either dried and packed for sale or further processed to produce boric acid and anhydrous borax. A long list of special products, including Boraxo, borate compounds, and both borax and boric acid of U.S.P. grade, also are produced.

In October 1955, Pacific Coast Borax Co. announced plans to convert its existing underground mining operations at Boron to an open pit operation and to construct



a new concentrator-refinery near the mine. The facilities at Wilmington will be retained for the production of boric acid and special products only. The initial stripping has been contracted to the Isbell Construction Company of Reno, Nevada. This phase of the work, which will take about two years, began in January 1956. Overburden, mostly sand and clay, will be removed with 18-cubic-yard rubber-tired scrapers to form a pit 2000 feet in diameter at the top and 150 feet deep. After the pit has been prepared, Pacific Coast Borax Co. will mine the ore with 3-cubic-yard electric shovels and 24-ton trucks. The ore will be broken with ammonium nitrate base explosives loaded in vertical blast holes made with auger type drills (Stern, J. D., 1956, personal communication).

A significant portion of California's borate production comes from Searles Lake, San Bernardino County. The processes used by the American Potash & Chemical Corporation and the West End Chemical Company to recover borax and other commodities from the complex Searles Lake brine are described in the introductory section to the salines in this volume.

Before the discovery of the sodium borate ores of the Kramer district, colemanite was the principal raw material from which borax was made. The mining of colemanite was comparatively expensive because, as mentioned above, the colemanite deposits typically are irregular bodies associated with incompetent, folded, and quite steeply dipping sediments. At Ryan, most of the ore was obtained from glory holes; but underground methods, including open stoping, shrinkage stoping, and square-set stoping were used elsewhere. Because colemanite is a friable mineral, blast holes were often made by hand drilling.

Because of the fact that colemanite decrepitates or flies to pieces when heated, the concentration of colemanite ore is comparatively simple. Colemanite ore was commonly heated to about 1300° F. in rotary calciners that contained an inner chamber to keep the ore from direct contact with the flame. By screening, the coarse material, mostly waste, was then separated from the fines, mostly decrepitated colemanite. This process was ineffective in recovering borates other than colemanite, and at least one plant contained jigs and Wilfley tables for recovering the borate values in the coarse product from the kiln.

Colemanite concentrates were shipped to a refinery for further treatment. There they were ground to a fine powder and digested with a hot sodium carbonate solution in reactor tanks provided with mechanical agitators. After several washings, the insoluble impurities and reaction products were removed and discarded; and the borax-rich liquor went to crystallizers where crystals of borax formed.

**Uses.** The three principal boron compounds of commerce, boric acid ( $\text{H}_3\text{BO}_3$ ), borax ( $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ ), and anhydrous borax ( $\text{Na}_2\text{B}_4\text{O}_7$ ) have such numerous and diverse applications that modern society could scarcely do without them. The ease with which borax can be melted and the solubility of most oxides in fused borax are properties valuable in ceramics and metallurgy. Because of its mild antiseptic and detergent properties, it may be an ingredient of soaps, cosmetics, dis-

infectants, and preservations. As a solvent of casein, it plays a part in the manufacture of glazed paper, plywood, and paint. Recently agricultural uses for borax have been developed. Some insecticides contain borax. Minute quantities of boron are essential for the healthy growth of plants, and borax in concentrations of up to 1/10th part per million is added to boron-deficient soils. Plants cannot, however, tolerate boron in concentrations of more than a few parts per million; and borax in large applications is an effective weed killer.

In California probably the largest single use for borax is in the porcelain enamel used on bathtubs, stoves, kitchen utensils, and metal signs. Porcelain enamel can contain as much as 20 percent  $\text{B}_2\text{O}_3$ . Another large use for borax in California is in special glasses such as glass wool which contain 12 to 14 percent  $\text{B}_2\text{O}_3$ . The common lime-soda glass used for bottles contains about one percent  $\text{B}_2\text{O}_3$ , but much if not all of it is added in the form of special borax-bearing soda ash produced at Searles Lake. Both colored and uncolored glazes for china and pottery contain boric oxide. Borax is the boron compound usually used, but colemanite is chosen if an insoluble borate is required. In addition, borax is commonly an ingredient of the fluxes used in welding, brazing, and soldering; and in metallurgy it serves as a flux in the refining of precious metals.

Elemental boron, organo-boron compounds, and the less familiar boron inorganics are the subject of intensive research. At present the consumption of these materials is small. Many compounds, however, are in the research or sales development stages; and their potential demand is great.

The consumption of elemental boron is probably less than 5000 pounds per year. One of its principal applications is in boron steels, which were developed during World War II and are now established materials. The addition of 0.001 to 0.003 percent of boron increases the hardenability of steel as much as far larger quantities of other hardenability agents and provides secondary benefits as well. Boron is being used with low alloy steels that normally have less than 5 percent of nickel, chromium, or molybdenum added to improve hardenability. Adding boron has made it possible to substantially reduce, but not completely eliminate, the proportions of other alloying agents required. Boron also is useful because of its ability to absorb neutrons. Atomic reactors are shielded with a material called Boral which consists of boron carbide and aluminum (Chem. Eng. News, Nov. 28, 1955). Potential uses of boron depend on its great hardness, unusual electrical properties, and affinity for gases. The use of boron as a deoxidizer in the metallurgy of copper is under investigation, and aluminum-boron alloys with low resistance have been developed that may be of value for electrical conductors. The potential demand for elemental boron may be as much as 2 to 3 million pounds per year (Chem. Week, Nov. 5, 1955).

Organo-boron compounds are being developed for use as dehydrating agents, synthesis intermediates, catalysts, plasticizers, and fire retardants for the petroleum, plastics, and other industries. The Standard Oil Company of Ohio is marketing a gasoline for high compression engines that contains a boron compound as an anti-knock agent (Hughes and others, 1956). Boron-phosphorus polymers and boron esters are under study; and one



ester, methyl borate, has been tested as a citrus fungicide. Some of the boron-hydrogen polymers, or boranes, have potential value as jet and rocket fuels.

The boron inorganics include such compounds as boron carbide, the metal borides, boron oxide, boron hydrides, and sodium polyborates. Boron carbide, one of the hardest materials known, is used as an abrasive and for abrasion-resistant articles such as sandblast nozzles. Borotherm, a product of American Potash & Chemical Corporation, is being used as a washable fire resistant additive for water base surface coatings and water base paint. Sodium borohydride is used as a reducing agent in the manufacture of hormones. The metal borides are resistant to heat, corrosion and wear; they have potential application both as coatings for metals and nonmetals and for tools and dies. Zirconium boride has been tested for use in jet and rocket nozzles.

**Prices.** The following prices f.o.b. plants were in effect in 1953:

Borax, granulated, 99.5 percent  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ , in sacks—\$41.25 per ton

Pentahydrate borax, in sacks, \$55.50 per ton

Anhydrous borax, in sacks, \$78.00 per ton

Borax concentrates, 34 percent  $\text{B}_2\text{O}_3$ , in sacks, \$32.75 per ton

Colemanite, ground, 30 to 40 percent  $\text{B}_2\text{O}_3$ , in sacks, \$47.00 per ton

Prices have since advanced slightly, and in December 1956 the price of granulated borax was \$43.25 a ton.

**Marketing.** The three principal borate producers in California, Pacific Coast Borax Co., American Potash & Chemical Corporation, and the West End Chemical Company, own or control their sources of raw materials. These companies distribute finished products, including both refined chemicals and crude sodium borate minerals beneficiated to varying degrees, through established channels that extend not only throughout the United States but into many foreign countries as well. In 1955, no refinery existed in the United States that purchased crude borate minerals. Of the three plants that produce borates, only that of Pacific Coast Borax processes crude sodium borate minerals. The grade of ore required for refining and for making beneficiated products is not generally known, but it is probably not less than 20 percent  $\text{B}_2\text{O}_3$ .

At present a small demand, probably only a few hundred tons a year, exists for colemanite, principally for ceramic use. Because of the high cost of treatment, colemanite cannot compete with sodium borate minerals or brines as an ore of borax even though the  $\text{B}_2\text{O}_3$  content of some colemanite ores is comparable to that of the sodium borate ores now used. Reserves of colemanite enormously greater than the present demand exist in mines of Pacific Coast Borax Co. and the West End Chemical Company that were worked on a large scale prior to the discovery of the Kramer deposits. The playa deposits are not of present economic interest. Not only are they small, irregular, and low grade, but if ulexite is present the cost of treatment is high.

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FIGURE 4. Aerial photograph showing new open pit and concentrator-refinery of Pacific Coast Borax Company Division, United States Borax & Chemical Corporation at Boron. Photo was taken while stripping of overburden and construction of the plant was still in progress. Approximately 10,000,000 tons of overburden are being removed with 18 cubic-yard rubber-tired scrapers. The pit is 2,000 feet in diameter at the top and about 150 feet deep. *Photo courtesy Mining World.*



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## BROMINE

BY WILLIAM E. VER PLANCK

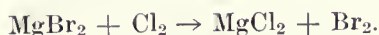
Bromine and bromine compounds are produced in California at a rate of about 1000 tons a year. Present sources in the state are Westvaco Chemical Division of Food Machinery and Chemical Corporation at Newark, Alameda County, which produces bromine from salt works bittern, and the American Potash & Chemical Corporation which obtains it from the brine of Searles Lake, San Bernardino County. Bromine is a by-product at both plants. California's output is about 2 percent of the national total. The principal source of bromine in the United States is a plant at Freeport, Texas, that treats sea water. Bromine is also recovered from well brines in Michigan, Ohio, and West Virginia.

**Geology and Mineralogy.** Bromine, one of the halogens, is intermediate in chemical properties between chlorine and iodine. At atmospheric pressure and normal temperature it is a heavy, reddish-brown liquid which is very volatile and corrosive. It usually is associated with the salines and is not found uncombined in nature. The saline minerals carnallite and sylvite contain bromine as an impurity. Sea water contains 0.0065 to 0.0070 percent bromine, which becomes concentrated in natural and artificial bitterns. Bromine is thought to be present in sea water in the form of magnesium bromide. The silver ore minerals bromyrite ( $\text{AgBr}$ ), embolite [ $\text{Ag}(\text{Br}, \text{Cl})$ ], and iodobromite ( $2\text{AgCl} \cdot 2\text{AgBr} \cdot \text{AgI}$ ) contain bromine but are not commercial sources.

**Methods of Recovery.** The Westvaco Chemical Division at Newark recovers bromine and other compounds from bittern obtained from the neighboring solar salt plants of the Leslie Salt Co. The bittern at a specific gravity of 30° Bé contains 0.175 percent bromine. Bromine is recovered from the bittern by a modified Kubienschky process, and the effluent from the bromine plant is treated for the recovery of magnesium compounds and gypsum as described in the section on magnesium and magnesium compounds in this bulletin.

Bittern, which is received only during the fall months, is stored in ponds of 200,000,000 gallons capacity. Raw bittern is neutralized with concentrated sulfuric acid and run into concrete storage tanks that hold several days' supply.

The bromine towers, of which there are three, are square, hollow columns built of stone and loosely packed with ceramic ware. Bittern, which has been preheated, is fed in at the top, steam at the bottom and chlorine gas at an intermediate point. Bromine is liberated according to the reaction



Ninety-five percent of the bromine in the bittern is recovered. Hot bromine-free liquor is drawn from the base of the tower, while from the top comes a vapor containing bromine, a little chlorine, and water. The vapor goes to a stoneware condenser where the water and

crude bromine are separated by gravity. The crude bromine is purified by distillation.

The American Potash & Chemical Corporation at Trona obtains bromine by a similar process from the brine of Searles Lake, which contains 0.085 percent bromine. In the main plant process, which is described elsewhere in this volume (see section on the salines), potassium bromide crystallizes isomorphously with potassium chloride; and both salts are recovered together. The saturated solution of the bromine-bearing potassium chloride, which contains 1.8 percent bromine, is neutral and requires no acidification before treatment in Kubienschky towers. The liberated bromine vapor passes through tantalum-lined condensers and is purified to give bromine 99.5 percent pure.

**Uses and Prices.** Most bromine is consumed in the form of bromine compounds. Ninety percent of the bromine produced in the United States is used in making antiknock gasoline, and minor amounts are used for pharmaceuticals and in photography. Much of the bromine produced in California is used as grain and soil fumigants in the form of ethylene dibromide and methyl bromide. Some is used in the form of bromochloromethane in fire extinguishers, and additional amounts are consumed as sterilizing agents for swimming pools and as an algicide in industrial cooling towers. With the exception of the ethylene dibromide used in antiknock gasoline, all of the bromine consumed in California is produced in the state.

The following prices were in effect in California in 1955: 225 pound drums, carload lots, delivered, 31-33 cents per pound. 6½ pound bottles, in cases, delivered, 39 cents per pound.

**History of Operations.** Bromine was produced for the first time in California in 1926 when the California Chemical Corporation, a predecessor of Westvaco Chemical Division, built a Kubienschky tower at Chula Vista, San Diego County. Bromine production from this plant, which treated salt works bittern, ceased in 1945. A second bromine tower was operated by the California Chemical Corporation at San Mateo from 1926 until late 1929 or early 1930, and it also treated salt works bittern. Westvaco Chemical Divisions' present bromine plant at Newark was built by the California Chemical Corporation in 1931. Production of bromine at Searles Lake began in 1940.

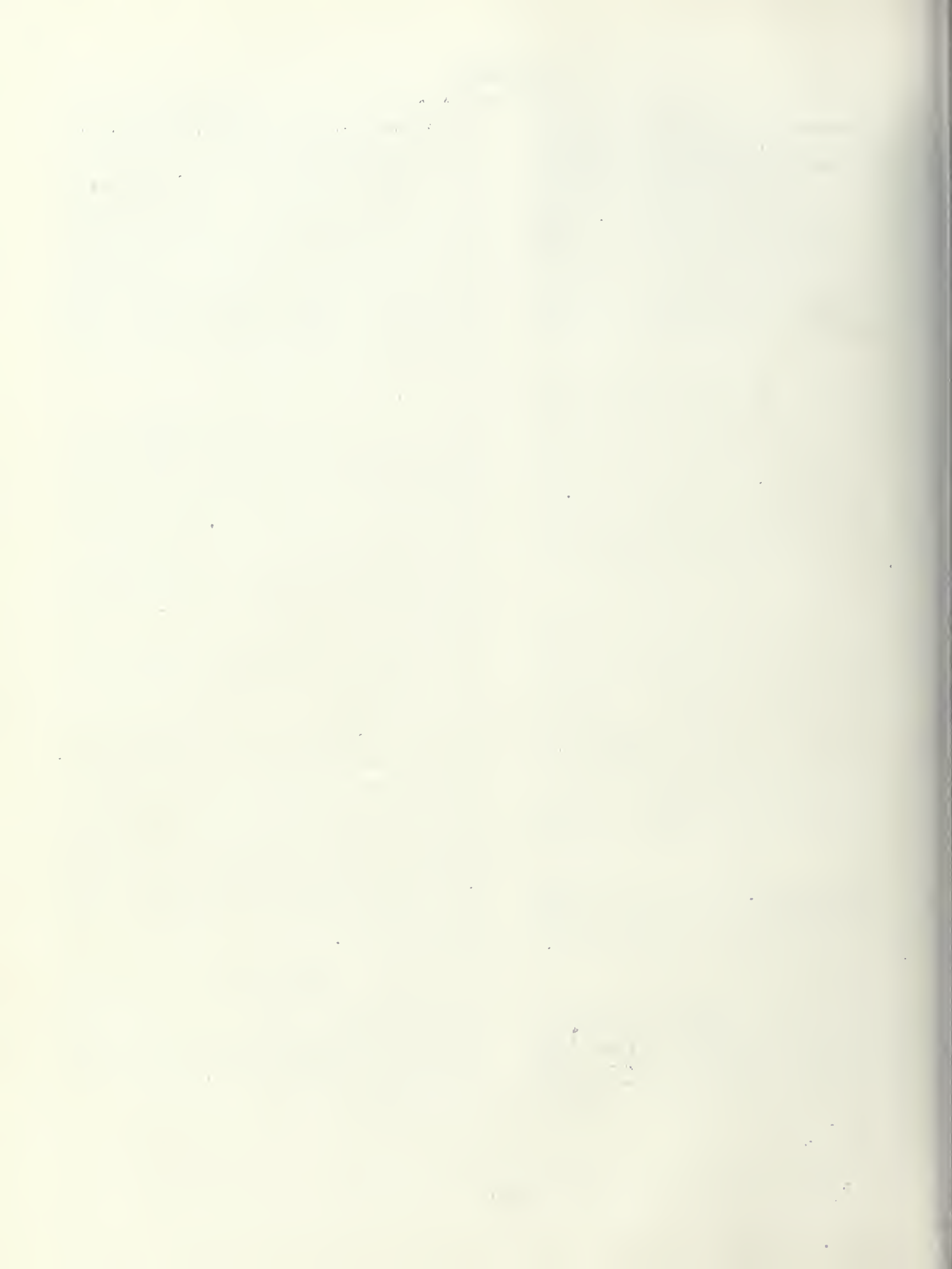
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## CADMIUM

By J. GRANT GOODWIN

Although cadmium is a metal of extreme usefulness in metallurgy, it has never been found in sufficient concentration to warrant mining where no other valuable material exists. Smelters seldom pay for it, often penalize for it, and commonly do not report its presence at all. Consequently cadmium is of little interest to the miner and often goes unmentioned in mine descriptions. In California, cadmium has been recovered from the lead-zinc ores of Inyo and San Bernardino Counties, and the copper-zinc ores of the Sierra Nevada foothills and Shasta County.

**Mineralogy and Occurrences.** Greenockite (cadmium sulfide) and xanthochroite (amorphous cadmium sulfide), the chief cadmium-bearing minerals, invariably occur with sphalerite (zinc sulfide), and cadmium in the form of cadmiumoxide (cadmium oxide) and otavite (cadmium carbonate) is therefore present in the oxidized portions of zinc sulfide bodies. Xanthochroite is the most commonly recognized cadmium mineral because it occurs as a conspicuous yellow coating on sphalerite.

Refined metallic cadmium is white with a bluish tinge. It is a soft metal with a hardness of 2.0. Its crystal structure is close packed hexagonal and the specific gravity is 8.7. The atomic weight is 112.4, melting point  $21^{\circ}\text{C}$ . ( $610^{\circ}\text{F}$ .), boiling point  $778^{\circ}\text{C}$ . ( $1432^{\circ}\text{F}$ .), and the heat of fusion 13.03 calories. The specific heat at  $0^{\circ}\text{C}$ . is 0.0548, specific resistance is 6.94, electrical conductivity is 22.7, and its thermal conductivity at  $0^{\circ}\text{C}$ . is 2200. Cadmium has a tensile strength of approximately 3,500 psi, and an elongation of 45 percent. It can be drawn into wire or beaten into foil. The chemical behavior of cadmium is similar to zinc. It is soluble in dilute acids, combines readily with halogens, and is easily alloyed with the common metals.

Zinc concentrates obtained in the milling of ores from deposits in the Rocky Mountain district average about 0.2 percent cadmium. Zinc concentrates obtained from ores of the Tri-state district (Missouri, Kansas, and Oklahoma) average 0.35 percent cadmium. In California, zinc concentrates from copper-zinc massive sulfide deposits and also from lead-zinc replacement deposits contain from 0.22 percent to 0.28 percent cadmium. California's principal cadmium production has been from the lead-zinc ores of Inyo and San Bernardino Counties, and from the copper-zinc ores of the Sierra Nevada foothills and the Shasta County copper-zinc district.

The estimated total production of cadmium from California ores, most of which were smelted outside the state, has been over 1,000,000 pounds since 1848 (based on the total estimated zinc production since 1848). The bulk of this production has been obtained since World War I. In recent years deposits in California have yielded annually about 70,000 pounds of cadmium from about 17,500 tons of zinc concentrates. The current annual production of cadmium in the United States is about 9,000,000 pounds, much of which is obtained from foreign ores smelted locally.

There are five major sources of cadmium: (1) cadmium-bearing flue dust from base-metal smelters, (2) cadmium-bearing flue dust from lead blast furnaces (most lead concentrates and ores unavoidably contain some cadmium-bearing zinc), (3) cadmium-bearing flue dust from zinc retorts, (4) high-cadmium precipitate obtained in purifying zinc electrolyte at electrolytic zinc plants, and (5) secondary cadmium metal recovered from bearings and other cadmium-alloy machinery parts.

Primary metallic cadmium is produced at about 13 zinc smelters in the United States. Most of the zinc ores and concentrates produced in California leave the state to be smelted elsewhere; however, some cadmium flue dust is recovered at the American Smelting and Refining Company plant at Selby. Flue dust collected in the bag house of this plant contains from 10 to 15 percent cadmium. Periodical shipments are made to the company's Globe Plant in Denver. Here cadmium-bearing flue dust, from all of the company's western smelters, is refined. Pure cadmium in stick and ball form is shipped to distributors throughout the world. The major supplier of cadmium in California is Federated Metals Division of American Smelting & Refining Company.

**Utilization.** Cadmium is widely used in the electroplating industry because it forms an adhering bond between iron and the plating metals. Cadmium alloyed with nickel or silver and copper is used in the fabrication of high-pressure, antifriction bearings. Cadmium plating on iron is superior to zinc for many uses. Lesser uses for cadmium are in the manufacture of stereotype plates, low-melting-point alloys such as solder, and automatic fire-sprinkler systems, for hardening copper, making silver resistant to tarnish in the manufacture of green gold, chemicals, photographic materials, paint pigments, rubber, soaps, and pyrotechnics, in textile printing, and as a pigment in glassware and enamels. The sulfide of cadmium is used in superior quality yellow paints. Cadmium oxide-silver contacts now being used in a wide variety of electrical devices promise improved life and performance with less tendency to weld together during arcing.

The largest consumer of cadmium in California is the electroplating industry. Several tons of cadmium in ball form, for anodes, are purchased each month by this industry. The manufacturers of calculators and other business machines in California consume each month about 1 ton of cadmium in stick form to be used in stereotype metals. California's airplane industry is fast becoming a large consumer of cadmium for high-friction alloys.

In recent years the production of cadmium from California zinc ores and concentrates has been about equal to the consumption of cadmium metal in California. The closing of two of the largest zinc producing mines (Shoshone mines in September 1953 and Darwin mines in February 1954) greatly reduced California's production during 1954. During 1955 these mines were reopened.

**Prices and Markets.** The demand for cadmium since World War II has increased rapidly and has forced the



price from 90 cents per pound in 1946 to \$2.00 per pound in 1949. During 1950 and 1951 the average market price was \$2.50 per pound. The apparent shortage and rise in price was caused in part by purchasing for the national stockpile and curtailment of uses in industry by the National Production Authority as a necessary measure to insure a substantial stockpile of this critical metal. With the incentive of high prices, imports in 1952 rose to more than 16 times the 1951 imports and as a result, the market price fell to \$2.00 per pound. During 1952 the Federal Government relaxed the controls on cadmium allocations and the market price fell still farther. By August 1954 the market quotation was \$1.70 per pound. The price remained at this level during 1955. As indicated above, the price of cadmium is of little concern to the producer of cadmium-bearing ores. Smelters seldom pay for it as the cost of recovery is high and the actual amounts contained in most ore shipments are low.

Recent trends which may affect the cadmium situation are: (1) the important place cadmium occupies in nuclear physics as a heat-control element in atomic reac-

tors, (2) the use of cadmium-nickel batteries which are superior to lead storage batteries, and (3) the substitution of other materials in the older, more established uses of cadmium. High prices force the use of substitutes and a market may be lost entirely. For example, during periods of shortage and high prices the electroplating industry can substitute zinc for cadmium; when supplies are again available, industry is reluctant to change back because of the expense and the threat of a future shortage. Cadmium compounds in pigments have been largely replaced by cheaper organic compounds. Over a long period new uses and greater demand generally offset the loss of markets to cheaper substitutes.

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## CALCITE

(Optical Grade)

By LAUREN A. WRIGHT

Transparent and unflawed calcite, from which polarizing prisms can be made, is employed in several types of optical instruments. Previous to World War II, it is probable that no more than 200 pounds of such material was used annually in the United States, and virtually no lightly colored (sub-optical) calcite was used. In 1943 and 1944, however, an acute demand developed for both types. The lower-quality material was used in the manufacture of optical ring gun sights. After 1944, however, the consumption of both types dropped sharply, and in the mid-1950's only about 100 pounds was being used annually in the United States. This drop was caused partly by the substitution of polaroid for the optical objects made of calcite.

The domestic production of calcite of both optical and sub-optical grade has been confined to a few localities in the western United States including two in California, but none of the deposits has proved large enough to support a continuing mining operation.

**Mineralogy and Geologic Occurrence.** Calcite ( $\text{CaCO}_3$ ) is one of the most common minerals (see section on limestone, dolomite, and lime products in this volume), but rarely does it occur in large, transparent crystals suitable for use as an optical material. Such calcite commonly is called Iceland spar or is designated as optical or sub-optical calcite, depending upon quality.

Calcite is characterized by a perfect rhombohedral cleavage at an angle of  $75^\circ$  and a hardness of 3. It will effervesce vigorously in dilute hydrochloric acid. The highest quality Iceland spar must be transparent, water-clear, and free from cloudiness, microscopic inclusions, cleavage cracks, and twinning. It must occur in masses large enough to yield cleavage rhombohedra about one cubic inch in volume. The Iceland spar that has been designated and sold as "suboptical" has been held to the same specifications as optical calcite except that a faint color or cloudiness has been tolerated.

Deposits of Iceland spar occur as discontinuous veins and pockets that rarely can be traced laterally or downward for more than a few tens of feet. Most of them exist in areas of Tertiary or Quaternary volcanism; many are enclosed in the volcanic rocks themselves, and appear to have formed at shallow depths during the end stages of the volcanism. The calcite apparently has grown unobstructed into open cavities and fissures. It is commonly accompanied by a red clay which appears to have altered from the enclosing rocks. Calcite veins are very abundant in most formations of limestone, but such vein material is almost invariably opaque or semi-opaque, and apparently has not yielded calcite of optical grade.

Iceland spar has been mined at many places throughout the world, but no single deposit has proved large enough to sustain a formal mining operation for more than a few years. Since the late 1930's most of the domestic requirements for Iceland spar have been supplied from deposits in the states of Sonora and Chihuahua, Mexico (King 1946 and 1947; Fries 1948). In these deposits the calcite occurs in cavities in young volcanic

rocks. Only about one-twentieth of the mined material has been trimmed to acceptable grade. The domestic production of Iceland spar has been obtained mostly from deposits in Montana, California, and New Mexico, but none of these sources has been active in recent years.

**Localities in California.** Iceland spar has been mined at two localities in California, one in eastern Modoc County and the other in northeastern San Diego County. The Elzie Bagley mine, in the Warner Range of Modoc County, and about 10 miles south of Cedarville, was worked intermittently during the period 1920-25, but has since been idle (Hughes, 1931; and Spangler Ricker, Engineer, U. S. Bur. Mines, personal communication, 1949). The calcite occurs as veins, from a few inches to as much as 3 feet in thickness, that lie in andesite of Miocene age. Some of the crystal aggregates are said to have weighed 60 to 80 pounds, but few, if any, individual crystals weighed more than 12 ounces. Most of the mined crystals were too flawed or too small to be of commercial grade, but the usable ones are reported to have been of excellent optical quality. The total output of the Elzie Bagley mine was small. About 1,000 ounces of Iceland spar were sold in the winter of 1920-21, which probably was the mine's most active period. The mine workings consist of a single open cut 25 feet long, 4 feet wide, and 15 feet in maximum depth.

The existence of the calcite deposits in northeastern San Diego County\* had been known for many years, but they were worked for the first time during World War II. They lie at the southern end of the Santa Rosa Mountains, about 7 miles west of Truckhaven on U. S. Highway 99. They are collectively known as the Hilton deposits and consist of four principal groups—the Central, Heather, Defiance, and Victory. Of these, the Central group has been the most productive.

The calcite occurs in pockets and vertical fissures in sandstone and conglomerate of the Palm Springs (Pliocene) formation. The fissure-fillings are discontinuously distributed along joints which are otherwise barren for most of their lengths. The largest and most productive calcite bodies have been found at joint intersections. None of the known calcite bodies proved to be more than 30 feet in maximum dimension. The calcite crystals are tabular and range from minute flakes to plates as much as 18 inches in diameter and 3 inches in thickness. As trimmed from the mined material, the usable plates have averaged between 2 and 3 inches in diameter and one-quarter to three-eighths of an inch in thickness.

The calcite was mined mainly by means of open cuts, the largest of which are about 30 feet deep. Although about 75 cuts exist in the four areas, many of them yielded little or no calcite, and all of them appear to have bottomed in barren rock. Numerous undiscovered calcite bodies, however, probably remain in the area.

\* The following information on the calcite deposits of San Diego County was obtained mostly from two sources: Durrell, Cordell, and Bell, G. L. Calcite mines in northeastern San Diego County, California: U. S. Geol. Survey Press Notice, Nov. 30, 1944; and Burgess, John A., Sonora, California, personal communication.



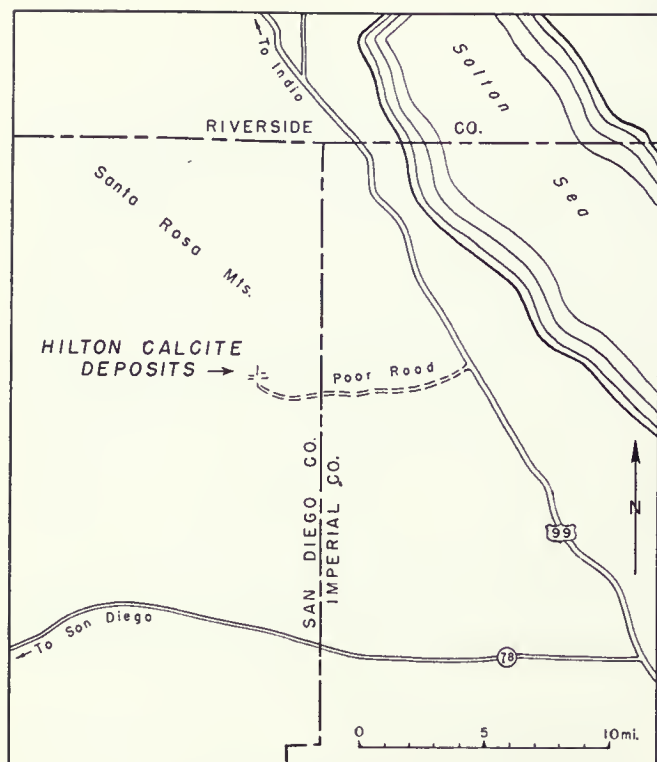


FIGURE 1. Map showing location of Hilton calcite deposits, San Diego County.

The Hilton calcite deposits were mined from late 1942 to early 1944. About 6,000 pounds of Iceland spar were shipped, but some of this output is said to have been non-usable. The acceptable material was used by the Polaroid Company in the manufacture of gun sights.

**Mining Methods and Treatment.** As deposits of Iceland spar have proved to be small and irregularly distributed, they have been worked by very small scale and short-lived operations. Most of the deposits in Mexico have been worked by the prospectors that have discovered them and who are experienced in the removal and sorting of the higher quality material. Hand methods are employed as blasting tends to produce cleavage cracks in calcite that would otherwise be of good quality. All of the calcite that is deemed likely to contain salable material is removed and carefully trimmed so that the largest possible rhombs of transparent and unflawed material are obtained. Trimming is done with a sharp-edged chisel which must be placed at skillfully chosen spots and struck sharply. The material that is deemed useful for optical purposes is first separated on the basis of ordinary visual inspection in daylight. It is later more carefully classified indoors with the aid of a thin pencil of light and under magnification.

**Utilization.** The usefulness of Iceland spar is based mainly on the property of double refraction. This causes light, which ordinarily vibrates in an infinite number of

planes, to be resolved into two rays as it passes through a calcite rhomb. Each ray vibrates in a single plane which is perpendicular to the plane of the other, and each has a different index of refraction. The Nicol prism is made from a single calcite rhomb. This is cut diagonally, ground and cemented together so as to cause one of the rays to be totally reflected and the other to be transmitted. Nicol prisms have been used as essential parts in polarizing microscopes, saccharimeters, polarimeters, and similar instruments. Optical calcite also was used in gunsights. In recent years polaroid, which is plastic sheet that contains oriented quinine sulfate crystals, has partially replaced Iceland spar in these uses. Certain consumers, however, still specify the Iceland spar.

**Marketing.\*** Although the domestic consumption of high-quality optical calcite is at present (1957) only about 100 pounds annually, a ready market still exists for such material. Its scarcity has led the principal producers of calcite optics to attempt to keep as much as several years' supply in reserve. Two firms—Crystal Optics, 4318 North Lincoln Avenue, Chicago 18, Illinois; and Bausch & Lomb Optical Company, 635 St. Paul Street, Rochester 2, New York, process optical calcite. Transparent calcite, unsuited to optical use, is purchased in small quantities by certain mineral dealers for resale to mineral collectors and schools. Three firms have been listed as dealing in optical calcite per se: Fish-Schurman Corporation, 70 Portman Road, New Rochelle, New York; John Schaad & Sons, Byberry Road above Philmont Avenue, Huntingdon Valley, Pennsylvania; and Schutte Optical Company, 16 Dowling Place, Rochester 5, New York.

The prices paid for optical calcite are nominal and are based mainly on the size of the unflawed, transparent rhombs. The current (1957) prices average about \$55 per pound. Much lower prices are paid for the poorer quality material which is used as specimens.

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\* Most of the following marketing information was kindly furnished by Mr. Nathan D. Golden, Director, Scientific Motion Picture and Photographic Products Division, U. S. Department of Commerce.



# CALCIUM CHLORIDE

BY WILLIAM E. VER PLANCK

In 1950, the production of liquid and flake calcium chloride totaled 21,875 tons (equivalent to 13,503 tons flake material containing 75 percent  $\text{CaCl}_2$ ) valued \$266,542. This was the largest recorded production of calcium chloride in California at that time; and, although more recent figures are not available, the production has risen steadily in the period 1950-55 and has tripled in the decade 1945-55 (Rogers, 1955). In recent years the production of calcium chloride in California probably has not exceeded 5 percent of the annual national total of the natural material, which has been in the range of 300,000 to 350,000 tons. The recovery of calcium chloride in the state is confined to a single playa, Bristol Lake, in San Bernardino County. This source supplies most of the calcium chloride consumed in southern California, and the Bristol Lake product also is marketed in adjacent parts of Nevada and Arizona.

Approximately half of the calcium chloride produced in the United States is obtained from natural brines, particularly in connection with the recovery of bromine and magnesia from brines in Michigan and West Virginia. The remainder is a by-product of ammonia-soda plants. An estimated 10 percent of the available supply is recovered in these operations.

**Geologic Occurrence.** Calcium chloride is a white, soluble, hygroscopic salt whose most common natural occurrence is in solution. Hexahydrated calcium chloride ( $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ ) is prepared by evaporating a calcium chloride solution at a temperature less than  $29^\circ \text{C}$ . ( $84^\circ \text{F}$ ). Four other hydrates can be prepared by partial dehydration of the hexahydrate, and the water of crystallization is completely driven off by heating to  $100^\circ \text{C}$ . The anhydrous salt can absorb more than its weight of water in 24 hours, and even calcium chloride solutions are hygroscopic.

Calcium chloride is present in the complex saline mineral tachydrite ( $\text{CaCl}_2 \cdot 2\text{MgCl}_2 \cdot 12\text{H}_2\text{O}$ ) and as an impurity in carnallite ( $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ). The only natural sources of calcium chloride that are of commercial

importance are certain comparatively uncommon terrestrial brines of the chloride type in which the amount of calcium approximates the amount of sodium. Magnesium is usually a minor constituent, but the concentrations of sulfate and carbonate are very low. In California, calcium chloride brines occur in Bristol Lake and Cadiz Lake, San Bernardino County, in the oil field brines of Ventura County, and in an artesian well on Mullet Island, Imperial County.

Calcium chloride has been obtained from Bristol Lake, San Bernardino County, since 1910; and at present Bristol Lake is the only commercial source in the state. In the past, some bittern from a salt works at Mullet Island near Niland, Imperial County, was sold as calcium chloride and used for sprinkling roads. The salt works obtained a portion of its brine from a well which presumably was the source of the calcium chloride. The Ventura County brine and the Cadiz Lake brine are relatively unfavorable potential sources of calcium chloride. The dissolved solids content of the Ventura County brine is less than that of average sea water. The Cadiz Lake brine is more concentrated, but calcium chloride forms a relatively low proportion of the dissolved solids.

**Bristol Lake.** Bristol Lake contains a number of salt beds intercalated with playa sediments. Salt is produced from the uppermost bed which is believed to be mineable over a 5-square-mile area. Throughout this area it averages 5 feet in thickness, and it is covered by an overburden that averages 5 feet in thickness. Calcium chloride is recovered from brine that seeps into excavations sunk through the topmost salt bed. The brine varies in both strength and composition in various parts of the lake and at different depths, but typically it contains calcium chloride and sodium chloride as the principal dissolved solids. Evidence from bore holes suggests that the calcium chloride-rich brine is largely confined to the uppermost 30 feet of the playa deposits.

*Analyses of some calcium chloride brines in California.  
(Percent of the dissolved solids.)*

	Bristol Lake <sup>1</sup>	Bristol Lake <sup>2</sup>	Cadiz Lake <sup>3</sup>	South Mtn. field <sup>4</sup>	Mullet Is. <sup>5</sup>
Cl.....	61.95	60.99	60.82	62.75	61.8
SO <sub>4</sub> .....	0.08	0.61	0.38	--	0.2
CO <sub>3</sub> .....	--	--	--	--	0.3
SiO <sub>2</sub> .....	0.01	0.05	--	--	--
NO <sub>3</sub> .....	--	--	--	--	1.0
Na.....	20.55	26.86	30.71	18.10	18.6 (incl. K)
K.....	1.18	0.86	1.41	--	--
Ca.....	15.52	10.02	6.12	18.52	14.5
Mg.....	0.38	0.35	0.56	0.63	3.6
Sr.....	0.34	0.23	--	--	--
Dissolved solids, percent.....	100.00	100.00	100.00	100.00	100.0
CaCl <sub>2</sub> , percent of dissolved solids.....	27.9	17.1	7.36	3.01	9.91
	43.1	24.2	16.53	53.5	40 (approx.)

<sup>1</sup> Sample from "canal" of National Chloride Co. Recalculated from Durrell, 1953, p. 13, analysis II.

<sup>2</sup> Sample from shallow well in SE $\frac{1}{4}$  Sec. 6, T. 4 N., R. 12 E., SB. Recalculated from Durrell, Cordell, 1953, analysis I.

<sup>3</sup> Gale and Hicks, 1920, p. 418.

<sup>4</sup> Brine from oil well, Hudson and Tallafierro, 1925, p. 1078, analysis 17.

<sup>5</sup> Brine from artesian well. Recalculated from Coleman, 1929, p. 221.



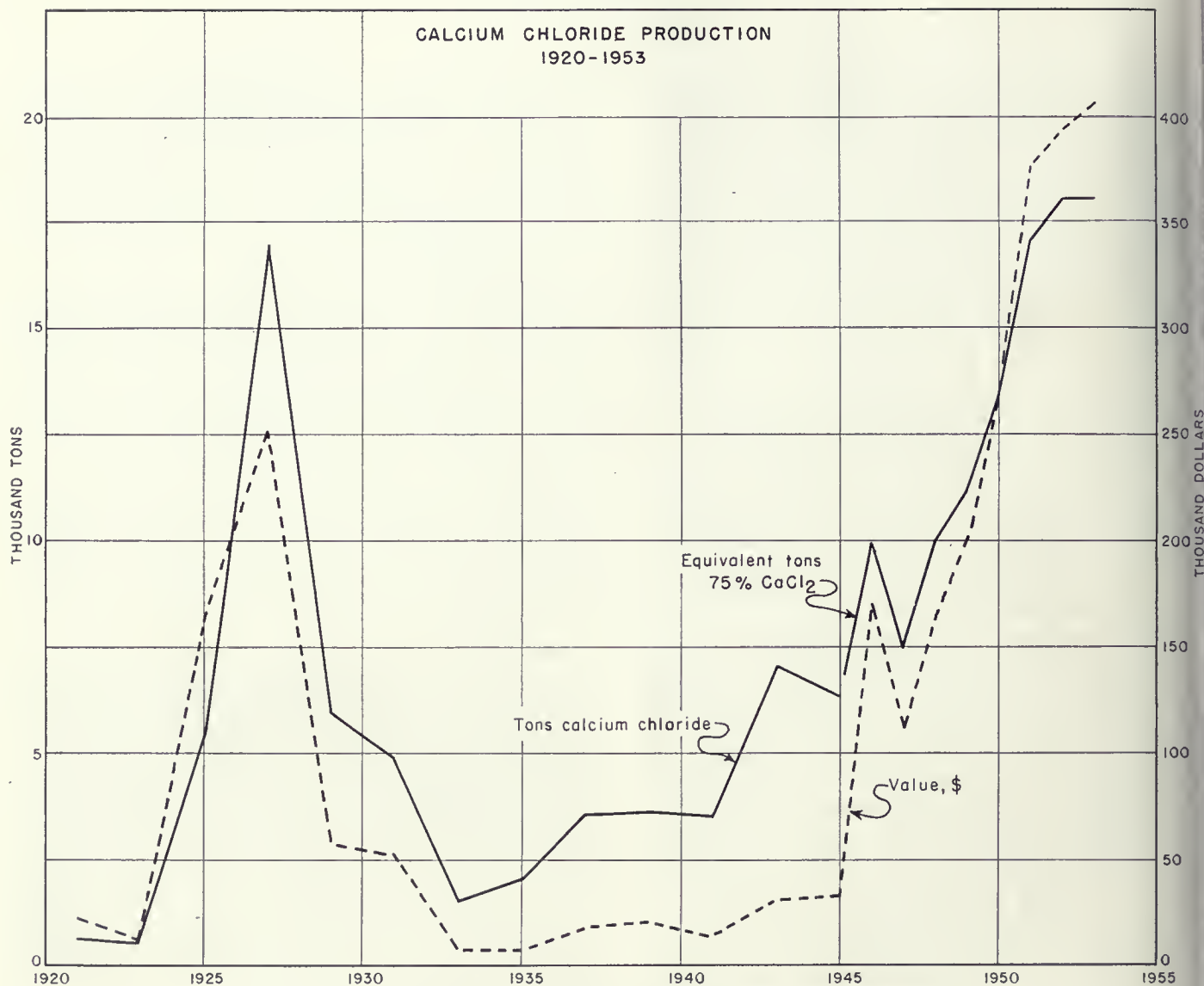


FIGURE 1. Chart showing the production of calcium chloride in California, 1920-53.

A calcium chloride-rich brine in a playa lake is unusual and must have formed under unusual geologic conditions. One possible source that has been proposed for the high calcium chloride content of the Bristol Lake brine is the volcanism associated with the Bagdad Crater, a Recent volcanic cone on the northwest margin of the playa (Gale, 1951, p. 10). According to another hypothesis, the calcium chloride is the result of a base exchange process in which calcium of the clay molecules in certain clay beds is exchanged for a portion of the sodium of a nearly pure sodium chloride brine (Rosenstein, Ludwig, personal communication, 1954).

Brines are collected by the California Salt Company and the National Chloride Company of America. The former employs pits from which the brine is gathered by tank truck, while the latter uses a system of "canals" or ditches with a total length of nearly 5 miles sunk into the mud beneath the first salt bed. The brine remains for some time in these pits and canals and is appreciably concentrated by evaporation. From time to time the

sodium chloride that precipitates in them must be cleaned out.

The brine is transferred to solar evaporation ponds at approximately 24° Bé and further concentrated. At 40° Bé, the practical limit of concentration by solar evaporation, the volume is reduced to one-sixth that of the brine pumped in, and almost all of the sodium chloride has precipitated. The sodium chloride is discarded. Much of the production is shipped as liquid calcium chloride in tank trucks or cars without further treatment. The rate of evaporation varies notably with the season and time of day. Ordinarily the evaporation of a pond requires between one and two months, although occasionally as little as two weeks is sufficient in the height of the summer. On winter days when evaporating conditions are poor the strong liquor sometimes extracts moisture from the air, and its specific gravity declines.

Hill Brothers Chemical Company purchases 40° liquor from one of the producers. A portion is resold, and another portion is converted to flake calcium chlo-



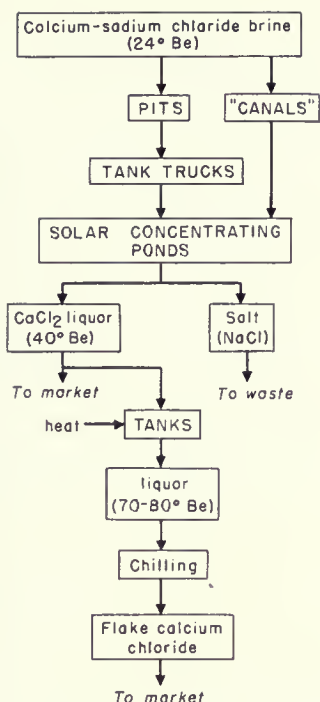


FIGURE 2. Flow chart showing method of recovering calcium chloride from Bristol Lake brine.

side which has a  $\text{CaCl}_2$  content of 73 to 75 percent. In the preparation of this material the 40° liquor is further evaporated by heating it to approximately 350° F. in boilers fired with oil burners; and the hot, saturated solution is chilled on a revolving, water cooled drum. Following drying and cooling steps, the flakes are packed in moisture-proof paper bags.

**Uses.** The uses of calcium chloride have developed mainly because (1) as an industrial chemical, it is a readily available soluble calcium compound; (2) it is hygroscopic; (3) the solution has a low freezing point —51° F.; and (4) solutions of calcium chloride have a relatively high specific gravity (a 40° Bé solution is one-third heavier than water).

As an industrial chemical, it is used in the recovery of certain metals from their ores and in the precipitation of calcium alginate in the manufacture of algin from sea weed. It is added to concrete to accelerate the time of setting, increase the early and final strength, aid curing, and improve the workability. A fraction of a percent of calcium chloride is sometimes added to the raw materials in cement manufacture to decrease the alkali content of the clinker. It is also applied as a method of weed control and soil compaction.

The low freezing point of calcium chloride has led to its use (1) as a brine medium in skating rinks and in the manufacture of ice and preparation of frozen confections; (2) as a medium for de-icing roads; and (3) as an antifreeze for fire barrels. As a hygroscopic material, it has proved useful in dehumidification of air, the fireproofing of foliage, the drying of walnuts, and control of dust on such surfaces as roads, construction yards, parking lots, and playgrounds. Because of their high specific gravity, calcium chloride solutions are used

as a medium for oil-well drilling and as ballast in tractor tires.

Most of the calcium chloride marketed in southern California is used in the treatment of ore and sea weed and by the concrete industry. Significant quantities are used for dust control and refrigeration, and a comparatively minor amount is consumed in the drying of walnuts and in oil well drilling.

**Marketing.** The calcium chloride market in southern California and in nearby parts of Nevada and Arizona is supplied almost wholly by material, in both flake and liquid form, obtained at Bristol Lake. Such materials are sold as far north as Stockton. The market in northern California is supplied largely by flake and pelletized calcium chloride shipped from the eastern United States.

In the eastern United States calcium chloride is prepared in C.P. and U.S.P. grades. The commercial grade, 94 to 97 percent  $\text{CaCl}_2$ , is marketed in pellet form. Partly dehydrated calcium chloride is marketed in flake form. Eastern flake calcium chloride contains 77



FIGURE 3. Photo showing a "canal" for the collection of calcium chloride brine, Bristol Lake, San Bernardino County. Brine is transferred from these ditches to ponds where it is concentrated by solar evaporation to 40° Baume. At this density almost all of the sodium chloride has precipitated. Much of the 40° liquor is sold as liquid calcium chloride, and the remainder is made into flake calcium chloride.



to 80 percent calcium chloride and California flake 73 to 75 percent. Much calcium chloride is sold in the form of solutions of 36°-40° Bé.

Typical prices in the Los Angeles area in 1955 were as follows:

Desert Brand flake (California), 73-75 percent, 1 to 5 ton lots, \$65 per ton.

Eastern flake, 77-80 percent, 1 to 5 ton lots, \$84 per ton.

Anhydrous, commercial grade, 94 percent, 1 to 5 ton lots, \$86 per ton.

Liquid (California), 36°-40° Bé, 13 cents per gallon in quantities of 1000 gallons.

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# CARBON DIOXIDE

BY HAROLD B. GOLDMAN

All but a very small proportion of the naturally occurring carbon dioxide gas that has been produced commercially in California has been obtained from two fields, one near the Salton Sea in Imperial County and the other near Hopland in Mendocino County. The Mendocino County field was opened in 1936 and was continuing to be productive in 1955. The Imperial County field was active from 1932-1954. The total recorded production from these fields is about 3 billion cubic feet valued at about 3 million dollars.

Approximately 75 to 80 percent of the carbon dioxide produced in California is obtained artificially by manufacturing processes which extract the gas (1) from flue gases resulting from the combustion of fuels; (2) as by-products of plants which produce ammonia from the natural gas of oil fields; (3) from gases resulting from alcohol fermentation; and (4) from the burning of limestone.

Natural sources account for the remainder. Approximately 10 to 15 percent of the total carbon dioxide being produced is chemically extracted as a by-product from oil field gases and about 5 to 10 percent obtained directly from natural carbon dioxide wells.

Liquid, gas, and solid carbon dioxide produced in the United States in 1953 totaled 743,368 short tons valued at 41.3 million dollars of which 80 percent was in the form of dry ice (U. S. Bureau of Census, 1954). About 670,600,000 cubic feet (about 40,000 short tons) were obtained from natural sources in the United States in 1953; approximately a third of this total was produced from natural sources in California.

**Properties.** Carbon dioxide is a colorless, invisible, non-inflammable, odorless, inert gas. It is known to the coal miner as "black damp" often causing fatalities by smothering. The gas can be liquefied at 31.1° C. (87.8° F.) under a pressure of 73 atmospheres and solidified at -56° C. (-69.9° F.) under a pressure of 5.1 atmospheres. Cold liquid carbon dioxide under pressure, expanded rapidly into air will precipitate directly as a solid resembling snow, having a temperature of -78.3° C. (-109° F.). This snow, compressed into blocks is sold under the term of "dry ice." The solid is about 1.3 times as heavy as water and evaporates to form the gas without melting. Carbon dioxide as a solid is valued because of its dryness, relatively high specific gravity, refrigerating effect, low temperature, and insulating and desiccating action of the gas evolved (Shreve, 1950, p. 111).

Table 1. Physical properties of carbon dioxide (after Rook and Williams, 1942, p. 14.)

Density as a solid (dry ice at -109.3° F.)	97.56 lb. per cu. ft.
Density as a gas at 32° F. and 1 atm. pressure	0.12341 lb. per cu. ft.
Specific gravity (air = 1)	1.52
Temperature of solid (dry ice) at 1 atm.	-78.3° C. (-109.3° F.)
Refrigerating effect due to change of state from solid to gas	275 B.T.U. per lb.
Critical point	31.1° C. (87.8° F.) & 73 atm. (1069.9 lbs. per sq. in.)
Triple point	-56° C. (-69.88° F.) & 5.1 atm. (75.13 lb. per sq. in.)

794,642 cu. ft. of CO<sub>2</sub> gas = 1 cu. ft. solid CO<sub>2</sub> and 16,285.39 cu. ft. of CO<sub>2</sub> gas is required to make 1 ton solid CO<sub>2</sub>.

**Origin.** Carbon dioxide occurs in nature in many volcanic gases, mineral springs and in subsurface reservoirs. It is an important accessory constituent of air and ocean, although present in fractional percentages. Clarke (1924, pp. 50, 148) estimates that, at 3 parts in 10,000, the carbon dioxide in the atmosphere amounts to about 2,200 billion tons, whereas the 44 milligrams per liter of carbon dioxide in the ocean would total about 25 times the amount in the air. However, these percentages are too small to permit a commercial extraction of the carbon dioxide from either the air or ocean.

Carbon dioxide is present in various concentrations in many volcanic gases and appears to be the normal product accompanying the last stages of volcanic activity. Volcanoes or igneous masses contribute gases to the atmosphere, ocean, ground water and accumulations form underground where there are favorable structural traps. All igneous rocks contain gases which are evolved when strongly heated in a vacuum. Analyses of these gases show that the principal constituents are: water, carbon dioxide, and hydrogen with subsidiary concentrations of carbon monoxide, nitrogen, methane and hydrogen sulfide (Quinn and Jones, 1936, p. 24).

Table 2. Percent by volume of carbon dioxide, nitrogen and oxygen in various volcanic gases (Quinn and Jones, 1936, p. 24).

Source	Date	CO <sub>2</sub>	N <sub>2</sub>	O <sub>2</sub>
Hawaii, the crater	1912	62.3	13.8	0.0
Vesuvius, edge of great crater	1865	4.8	75.6	19.6
Phlegrean Fields, Torre del Greco, Flow of 1694	1869	90.2	6.2	0.08
Etna, Crater B, fumarole	1865	5.0	77.28	17.27
Sicily, Salinella of Paterno Aequa Rossa	1856	97.9	2.1	--
Lipari Isles, Vulcano, near the chemical works	1856	86.0	14.0	--
Santorin, Port of George	1870	98.8	1.8	0.4
West Indies, Guadeloupe fumarole of the north	1904	52.8	36.07	7.5
Colombia, S. America, Purace Solfatara	1868	98.2	--	--
Iceland, Krisuvik, second fumarole	1846	88.24	0.69	--
Katami, Ten Thousand Smokes, Nora Rupta Basin	1919	70.4	12.8	1.0
Canary Island, Pico de Teyde, south fumarole	1907	71.1	26.9	--

Accumulations of carbon dioxide may have formed by the action of igneous rocks at depth, coming in contact with limestones, dolomites, coal or organic matter and driving off the gas as a direct result of heat (Miller, J. C., 1933, p. 19).

Gas in springs may be caused by the action of acidic waters on carbonates of sodium, calcium and magnesium. Miller (1933, p. 19) suggests that, aside from these inorganic sources, which are the results of igneous and chemical activity, carbon dioxide may also be the product of organic decay. The common association of carbon dioxide with hydrocarbons in sedimentary rocks indicates that organic matter was present in the producing or adjacent strata. Many wells drilled for oil give off large quantities of carbon dioxide with the oil. Natural gases containing high percentages of carbon dioxide occur in the western states: Colorado, Utah, New Mexico, Washington, Oregon and California; and in other coun-



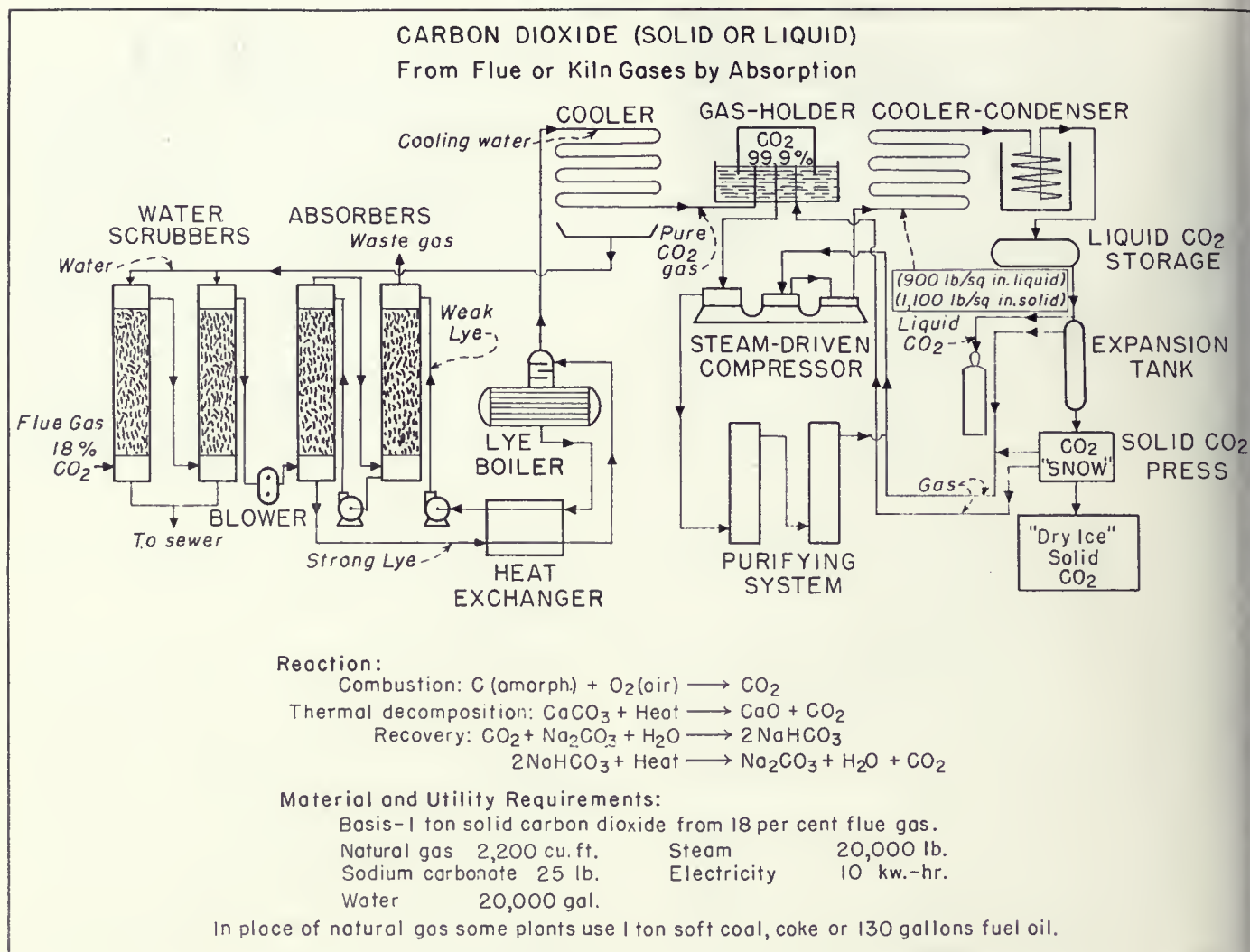


FIGURE 1. Flow sheet showing production of carbon dioxide from flue gas.

tries: Tampico, Mexico; Alberta, Canada; and New Plymouth, New Zealand.

**Occurrences in California.** Carbon dioxide was first produced commercially in California in 1894 from a gas-filled drift on the 575' level of the New Almaden mine in Santa Clara County. The drift was sealed off and the gas drawn off through a pipe in the bulkhead. This gas was compressed and used to manufacture soda water. Production stopped in 1896. There is no record of carbon dioxide being produced from 1896 until 1933 when the Imperial County field was developed.

The Imperial County gas field, about 4½ miles southwest of Niland at the edge of the Salton Sea, was active from 1932-1954. In this area carbon dioxide occurs at shallow depths in Quaternary alluvium composed of sand and clay. The original source of the gas seems to be related to igneous activity. According to magnetic studies (Kelley and Soske, 1936, p. 506), the entire area is underlain by a batholithic mass. Recent volcanism, marked by volcanic domes and mud pots, suggests that the mass is still consolidating. The wells appear to be aligned with the southeasterly projection of the San

Andreas fault which may well have been the means by which the carbon dioxide gas migrated into the overlying sediments (Rook and Williams, 1942, p. 27).

In late 1932 the original discovery well was drilled in sec. 12, T. 11 S., R. 13 E., S. B. B. & M., by the Salton Sea Chemical Products Corporation. Remarkably pure carbon dioxide gas (99.1 percent) was encountered at 750 feet in considerable quantity, but no commercial use was made of the gas from the well. Another well was drilled in 1933, and produced sufficient gas to permit the company to install a pilot plant to manufacture dry ice. The first commercial plant was completed about August 1, 1934. Salton Sea Chemical Products Corporation was dissolved in October, 1935, and the assets acquired by the Pacific-Imperial Dry-Ice Inc. This corporation operated the plant and properties until February, 1940, when it was acquired by the Natural Carbonic Products, Inc., which operated until 1944.

In 1934, Imperial Carb.-Ice Corporation drilled four wells in sec. 2, T. 11 S., R. 13 E., and sold the gas until 1937 to the Salton Sea Chemical Products Corporation. In that year the National Dry Ice Corporation acquired the assets of the Imperial Carb.-Ice Corporation and



Table 3. Analysis of high carbon dioxide natural gases from wells in the United States.<sup>1</sup>

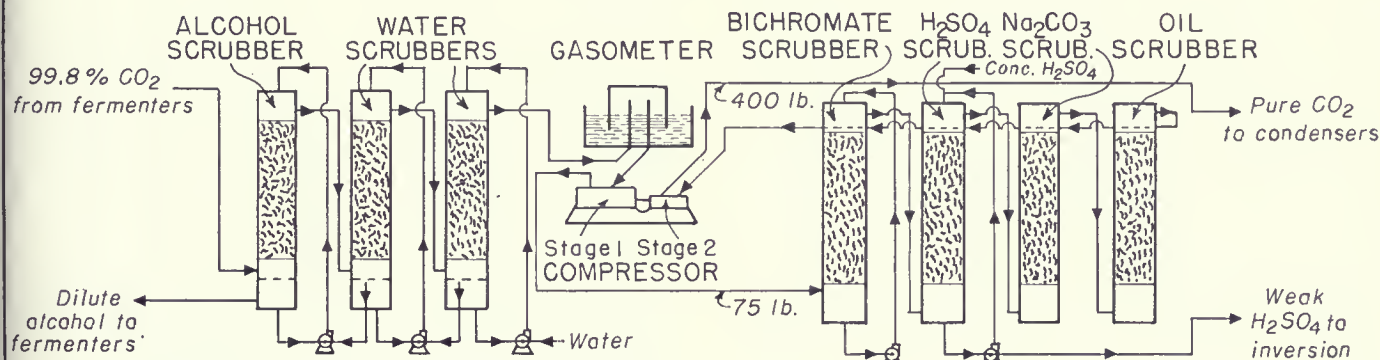
State	County	Field	Age of gas-producing formation	Depth of producing zone (in feet)	Initial daily flow per well (in thousands of cubic feet)	Initial pressure (pounds per square inch)	Percent methane (CH <sub>4</sub> )	Percent ethane (C <sub>2</sub> H <sub>6</sub> )	Percent carbon dioxide (CO <sub>2</sub> )	Percent oxygen (O <sub>2</sub> )	Percent nitrogen (N <sub>2</sub> )	Percent helium (He)
Colorado	Jackson	Walden <sup>2</sup>	U. Cretaceous	4875-5113	35,000	1,000	0.52	3.95	92.14	0.09	3.16	0.14
Colorado	Garfield	Carbonera	U. Cretaceous	2857-3769			65.00	4.20	20.00	0.40	10.40	
Colorado	Garfield	Carbonera	Jurassic ?				19.69	4.39	61.05	0.27	14.60	
New Mexico	Coffey	Jaritas Dome	Triassic	1509	500		0.00	0.00	67.20	4.10	28.70	
New Mexico	Mora	Wagon Mound	Triassic	1420	5,000	25	0.00	0.00	90.00	2.20	7.80	
New Mexico	Torrance	Estancia <sup>2</sup>	Pennsylvanian	1240-1340	200	432			97.94			
New Mexico	Harding	Bueyeros <sup>2</sup>	Triassic	940	3,600	36			98.20			
Utah	Emery	Woodside	Permian	3120	9,000	900	0.00	5.70	31.70	0.27	61.02	1.31
Utah	Carbon	Farnham <sup>2</sup>	Permian	3093	20,000	760	0.30		98.30		1.14	0.03
California	Kern	McKittrick <sup>2</sup>	Tertiary	1300-5000			66.20	1.00	30.40	0.00	2.40	
California	Kern	Kern River <sup>2</sup>	Tertiary	900			84.30	8.00	6.50	0.00	1.20	
California	Kern	Sunset <sup>2</sup>	Tertiary	1400-4800			87.70	0.00	10.50	0.00	1.80	
California	Kern	Sunset-Midway <sup>2</sup>	Tertiary	1400-4800			65.20	9.40	24.20	0.00	1.20	
California	Kern	Buena Vista Hills <sup>2</sup>	Tertiary	1400-4800			42.20	37.50	16.50	0.00	3.80	
California	Fresno	Coalinga <sup>2</sup>	Tertiary	1200-3000			88.00	0.00	11.10	0.00	0.90	
California	Santa Barbara	Santa Maria <sup>2</sup>	Tertiary	1100-4280			62.70	20.20	15.50	0.20	1.40	
California	Imperial	Niland <sup>2</sup>	Quaternary	200- 400 500- 700	60	80-100			99.10			
California	Mendocino	Hopland <sup>2</sup>	Jurassic	350 1700	40 1,940	30	1.75		97.0	0.75	0.50	

<sup>1</sup> After Dobbin, C. E., 1935, p. 1068.<sup>2</sup> Field from which carbon dioxide has been removed commercially.<sup>3</sup> Producing oil fields.

erected a dry ice plant in Niland. The National Dry Ice Corporation (now Cardox Corporation) operated in the field until April 1954. The entire field was continually developed from 1932-1954. By 1943 a total of 66 wells

had been drilled of which only half were completed as producers. Numerous additional wells were subsequently drilled as the average life of a well was from 1 to 2 years because of sand and precipitated calcium carbon-

### CARBON DIOXIDE FROM ALCOHOL FERMENTATION (Reich Process)



Reaction:

Yield - 1 bu. corn or 6 gal. molasses = 2 1/2 gal. ethyl alcohol (190 proof) and 17 lb. CO<sub>2</sub>

Material and Utility Requirements:

Basis - 1 ton solid carbon dioxide			
Potassium bichromate	0.5 lb.	Water	2,000 gal.
Sodium carbonate	0.01 lb.	Electricity	5.9 kw.-hr
Sulfuric acid (66°Bé)	6 gal.	Oil	0.01 gal.
Steam (pumps only-compressors)		20,000 lb.	

FIGURE 2. Flow sheet showing production of carbon dioxide from alcohol fermentation.



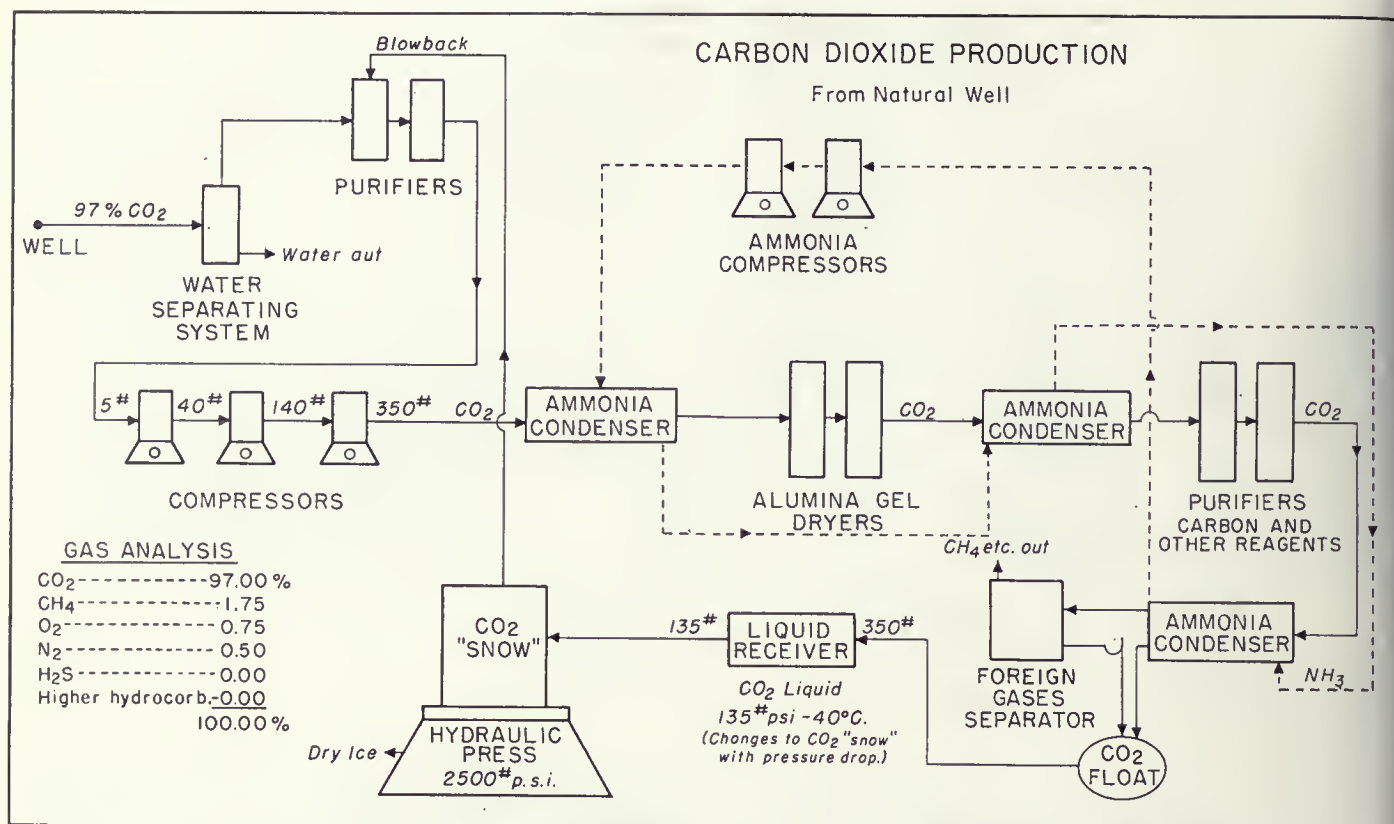


FIGURE 3. Flow sheet showing production of carbon dioxide from natural wells, Caldri Ice Corp., Hopland.

ate sealing the well perforations. Production was ultimately obtained from an area about 2 miles wide by 3 miles long. The original productive zone was 200 to 400 feet deep with the most recent production coming from a deeper zone 500 to 700 feet deep. In the early 1950s the addition of irrigation waters to the Salton Sea caused a rise in the water level. In 1954 this water encroachment was an important factor in forcing the one remaining producer, the Cardox Corporation, to abandon the field and seek a more convenient and economical supply of gas. Prior to abandonment in April 1954, 12 wells were in operation. A total of approximately 2½ billion cubic feet of carbon dioxide was produced from this field.

The Hopland carbon dioxide field in Mendocino County lies 2 miles north of the settlement of Hopland on the east bank of the Russian River. The gas occurs at depths of 300 to 1700 feet in rocks of the Franciscan formation. Wells were drilled near seeps in the Recent river alluvium at the edge of a landslide area of Franciscan graywacke, serpentine, and metasedimentary rocks. Approximately 50 feet of alluvial fill overlies an undifferentiated bedrock sequence of graywacke, chert, serpentine, shale, greenstone, and glaucophane schist. Examination of the electric log and the cuttings from the most recent well revealed three producing zones. A shallow zone, from which the earliest production was obtained, extends in depth from 300 to 500 feet in a sequence of chert and graywacke. An intermediate zone extends from a depth of approximately 670 to 820 feet in a sequence of graywacke and chert. The deepest zone

starts at 900 feet and extends to depths exceeding 1250 feet. The predominant rock types in the deep zone are sheared serpentine and graywacke. As much as 1000 gallons of water per minute are discharged with the gas at temperatures ranging from 140° to 185° F. The quantity of gas increases with depth, and in the deepest well (1700 feet) pressures up to 30 pounds per square inch are obtained. The lateral extent of the field is unknown, as exploration drilling is limited to the leased area of 1 acre. Theories about the origin of the gas are speculative. Recent volcanism related to that in the vicinity of Clear Lake, about 20 miles to the east, may be a possible source. Presumably the gas migrated into the porous



FIGURE 4. Natural carbon-dioxide wells, Caldri Ice Corp., Hopland.



Table 4. Principal sources of carbon dioxide in California.

Source	Percent of total production	(approx.) <sup>1</sup>
Natural		25
Wells that produce CO <sub>2</sub> as principal gas	5-10	
Oil field containing 16 percent CO <sub>2</sub> in natural gas <sup>2</sup>	10-15	
Manufactured		75
By-product from ammonia plants (natural gas used as raw material)	35-40	
Flue gas recovery from burning natural gas	35-40	
By-product of alcohol fermentation	1-2	
Burning of limestone	Captive use <sup>3</sup>	

<sup>1</sup> Estimated from plant capacities.<sup>2</sup> For other California oil fields that report high carbon dioxide content see table 3.<sup>3</sup> West End Chemical Company, Searles Lake, produces carbon dioxide for own use in chemical manufacturing.

zones of highly fractured and sheared rocks which also contain considerable quantities of ground water.

The discovery well was drilled in 1931 by the Caldri Ice Corporation, Old River Road, Hopland. The well, 300 feet deep, produced approximately 40,000 cubic feet per day of 97 percent pure carbon dioxide gas. A plant was subsequently built by the Caldri Corporation at the site of the well. In 1936, the first year of production, about 6 million cubic feet of carbon dioxide was produced. The gas had to be vacuum pumped from the well and the desire for a greater yield and higher gas pressure caused the owners to drill additional and deeper wells. In 1950, 6 wells 350 feet deep, 10 and 8 inches in diameter and one well 790 feet deep, 12 to 8 inches in diameter were active. The most recently drilled well (1700 feet) has a capacity of almost 2 million cubic feet a day. This well yields, in addition to gas, 1000 gallons per minute of water at 140° F. A total of fifteen wells have been drilled in this field. All wells but one are capped and production is exclusively from the 1700-foot well. The gas is dewatered at the well and piped to the plant where it is dried, purified, compressed to liquid and transformed into solid dry ice. The solid is sawed, wrapped and shipped by truck trailer to northern California, Washington, Oregon, and Nevada. The plant, with all new equipment including a 2500-pound hydraulic press, is estimated to cost between half and three-quarters of a million dollars and can produce 30 tons a day. In 1956 Caldri became a subsidiary of the National Cylinder Gas Company. Since 1936 an estimated 600 million cubic feet of carbon dioxide gas has been produced from this field.

The Ukiah carbon dioxide field is the only other place in California where carbon dioxide has been recovered on a commercial basis, but its output has been very small. Two wells were drilled on the south side of Clay Street in the city of Ukiah by L. J. & Bess Gibson in late 1939 or early 1940. The first well was drilled to a depth of 235 feet and the gas shut in. The second well drilled to a depth of 465 feet flowed gas and water for a while but later had to be pumped. A processing plant at the site of the wells removed the water, filtered out the impurities, compressed and cooled the gas to a liquid for delivery in trucks. The plant has been idle since 1948 (O'Brien, 1953, p. 356).

In addition to the three fields already described, minor occurrences of carbon dioxide gas have been re-



FIGURE 5. Photograph showing hydraulic press manufacturing solid carbon dioxide (dry ice) at Caldri Ice Corp., Hopland.

ported from California. Gas from mineral springs in Lake County near Bartlett Springs has been used to recarbonate water (Averill, 1947, p. 19). A seep has been reported in a ravine north of Santa Cruz near the San Andreas fault zone (Hubbard, 1943a, p. 36).

**Production of Carbon Dioxide.** The basic processes involved in the commercial production of liquid or solid carbon dioxide consist of passing the gas through absorption systems to concentrate the gas, purification systems to remove odors and minor impurities, and compression and refrigeration systems to liquefy the gas.

Low grade gases (10 to 40 percent carbon dioxide) are removed from fine gases or natural oil field gases and are concentrated to over 99 percent by absorption systems. Aqueous solutions of sodium or potassium carbonate, monoethanolamine, or triethanolamine are used as absorbents from which the concentrated gas is recovered by heating.

Purification systems contain activated carbon, limestone, or silica gel to remove impurities such as sulfur dioxide and dust. Odors are eliminated by oxidizing the organic impurities in a potassium bichromate (or potassium permanganate) solution. Entrained water is removed by adsorption on silica or alumina gel, by refrigeration, and by sulfuric acid or calcium chloride dryers.

After concentration and purification the gas is compressed in two stages (400 to 500 lbs. per square inch) or three stages (900 to 1000 lbs. per square inch) and liquefied in condensing chambers that are ordinarily cooled by an ammonia system of refrigeration. The liquid carbon dioxide is removed from the condensing chambers and is stored or is piped to a "snow" chamber to be transformed into solid carbon dioxide (dry ice). The snow chamber is a cube-shaped hydraulic press with the upper and lower sides formed by rams attached to hydraulic cylinders. The liquid is released through a nozzle in the wall of the chamber under reduced pressure, which causes the liquid to change to snow. After sufficient snow accumulates the hydraulic rams compress the



Table 5. *Principal uses of carbon dioxide.\**

Solid	Transported in paper bags. Evaporation loss slight on large shipments and quick turnover.	<b>Refrigeration:</b> Used in the transport and storage of ice cream, meat, fish, fruit, and vegetables. <b>Heat and cold treatment:</b> Used in shrink fitting of machine parts and hardening steel alloys. <b>Laboratory:</b> Used in hydration of biological serums, freezing micro-sections. <b>Chemical:</b> Used as cheap non-corrosive acid anhydride that can be shipped without special containers and safely handled.
Liquid	Transported in heavy steel cylinders or bulk refrigerated tank cars. Small storage loss permits holding longer time.	<b>Refrigeration:</b> Used in compression refrigeration systems which are dependable in not endangering lives in case of leakage. <b>Blasting:</b> Used as explosive in coal mines. Expands more slowly and breaks coal cleaner than powder explosives. <b>Power:</b> Used as bottled power for same purposes as compressed air is used.
Gas	Not economically transported in small quantities. Shipped as solid or liquid and converted to gas for use.	<b>Carbonation:</b> Used to manufacture carbonated water, soda pop, and other sparkling beverages. <b>Preservation:</b> Prevents spoilage of certain canned goods because of oxidation, i.e. cocoa, coffee, powder milk, shredded coconut; and preserves fruits, vegetables, meat and flowers. <b>Fire extinguisher:</b> Used in extinguishing fires by lowering temperature and smothering the flame. Oxygen is reduced from 21 percent to 15 percent. <b>Chemical:</b> Used in the manufacture of carbonates, urea, salicylic acid. <b>Power:</b> Used as a source of power to project liquid spray into trees—will stimulate respiration of insects, making poisonous sprays more effective.

\* After Rook and Williams, 1942, pp. 15-16, and Quinn and Jones, 1936, p. 231.

snow into a solid block of dry ice which is sawed, wrapped and shipped.

Figure 1 is a flow sheet of a typical process used to recover carbon dioxide from the flue gases produced by burning coke and is applicable to other raw materials (fuel oil, natural gas, limestone) that yield a gas of low purity (10 to 40 percent carbon dioxide) (Faith, Keyes, and Clark 1950, p. 183).

The carbon dioxide gas obtained as a by-product from alcohol fermentation is so pure (99.5 to 99.8 percent) that the absorption portion of the previous process is not required. Figure 2 is the flow sheet of a typical process used to purify and liquefy carbon dioxide from alcohol fermentation (Faith, Keyes, and Clark, 1950, p. 186).

The treatment of the high carbon dioxide content gas from natural wells or the by-product gas from ammonia

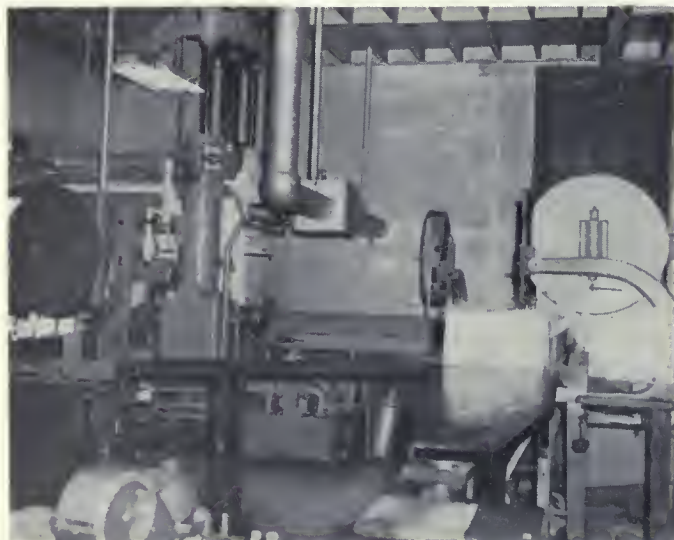


FIGURE 6. Equipment for the manufacture of dry ice, Caldri Ice-Corp., Hopland. The hydraulic press is in the left center. In right foreground dry ice is being cut on band saw.



FIGURE 7. Wrapping dry ice at Caldri Ice Corp. for shipment. Two thicknesses of paper wrapping are used.

plants ordinarily consists of oxidizing and drying the gas before compression. Figure 3 is the flow sheet of the operation of the Caldri Ice Corporation at Hopland; a plant that draws its gas directly from natural wells (Hubbard, 1943b, p. 304).

*Uses.* Ninety percent of the total production of carbon dioxide is used in the ice cream and soft drink industries. The ice cream industry uses solid carbon dioxide (dry ice) as a storage and transportation refrigerant because dry ice has the advantage over water ice in many respects, especially freedom from drip, extreme low temperature, and absence of residue. One pound of dry ice will substitute for 15 to 20 lbs. of water ice. For example, a railway refrigerating car going from coast to coast is filled with 8,000 to 11,000 lbs. of water ice and must have some of it replaced at least twice. One charging of 3,000 lbs. of dry ice is sufficient for 6 to 15



Table 6. Production of natural carbon dioxide gas in California.\*

Year	Thousands of cubic feet	Value	Year	Thousands of cubic feet	Value
1934	80	\$4,072	1944-1945	429,382	\$524,280
1935	800	12,000	1946	161,929	310,938
1936	81	1,300	1947	196,808	
1937	0	0	1948	168,813	
1933-1935	15,440	1,822	1949	165,089	
1936-1937	89,777	64,787	1950	168,999	
1938-1939	131,189	13,799	1951	196,171	
1940	97,660	23,877	1952	227,667	
1941	138,862	258,563	1953	214,663	
1942	193,143	310,000	1954	102,132	
1943	227,424	248,126			

From Annual summary of operations—Cal. oil fields, 1948-1954: California Div. Oil and Gas, vol. 40, no. 2, and Averill, King, Symons, H., and Davis, 1948, California mineral production for 1946: California Div. Mines Bull. 139, p. 64.

lays and requires only a fraction of the room used by water ice (Shreve, 1950, p. 111).

The bottling industry uses carbon dioxide gas to carbonate beverages. When the gas is dissolved in water, the solution contains a compound resulting from the combining of the gas with the water and the ions produced by the compound. The result is a sparkling liquid to which is added syrup and flavoring to produce a bottled beverage sold to the public as "pop."

Other important uses of carbon dioxide are based on (1) the property of the gas to reduce the percent of oxygen in the air, as in food preservation and fire extinguishing; (2) the power supplied by compression of the liquid, as in insect sprays and blasting devices; and (3) the refrigerating properties of the liquid and solid in the storage and transportation of food, and heat and cold treatment of metals.

**Markets and Prices.** Approximately 75 percent of the total carbon dioxide shipped in the nation is in the solid form as dry ice. In California, the proportion of solid to liquid shipped is approaching equality because of the increase in the industrial applications of bulk liquid carbon dioxide. Liquid carbon dioxide (in cylinders) has sold for the same price, \$0.06 per pound, from 1929 to 1956. Solid carbon dioxide sells for \$0.035 to \$0.04 per pound, a slight rise over the constant price of \$0.03 per pound from 1935 to 1949.

Carbon dioxide plants are ordinarily located close to centers of consumption to avoid transportation problems. However, bulk liquid refrigerated tank cars are economically shipped up to 400 miles; and solid carbon dioxide up to 200 miles. Liquid in cylinders is sold only in local distribution areas because of the freight expense involved in returning empty cylinders.

**Trend of the Industry.** Increased industrial application of new uses, as well as the normal demand for carbon dioxide, points toward continuing high levels of production. The trend is toward larger and more centrally located plants representing capital investments of hundreds of thousands of dollars. A large capacity hydraulic press, which before World War II cost \$22,000, now is worth up to \$70,000. In 1949 a small plant (6 tons a day) cost from \$12,000 to \$90,000. The newest manufacturing plants producing carbon dioxide from



FIGURE 8. Index map showing location of natural carbon dioxide fields in California.

the by-product of ammonia plants have capacities rated at 100 tons a day, while the average capacity of a flue recovery plant is 50 tons a day. This problem of heavy capitalization is one of the problems contingent to exploiting a natural source of carbon dioxide. Another factor of importance is the threat of competition from as yet undeveloped artificial sources such as the flue gases from cement plants, flue gases from steam plants, and the waste gases from oil refineries (estimated at 10,000 tons of carbon dioxide a day in California). Competition is keen and although costs have risen the price of the gas has remained constant.

The natural gas may have impurities such as the lighter gases that are difficult if not uneconomical to remove. Natural occurrences in areas of active faulting have an additional problem in possible earth movements that can reduce the activity or cut off the flow of gas from wells. For example, the Niland field at one time lost 6 to 8 wells with sheared casings after a mild earthquake.

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FIGURE 9. Automatic gas trap which was used in the now defunct carbon dioxide field at Niland, Imperial County. The carbon dioxide gas and water entered the trap through a flexible hose. The gas was liberated and the water accumulated in the trap chamber until its weight exceeded that of the counterbalance, causing the chamber to move downward and open a valve permitting a portion of the water to be expelled through an orifice in the bottom of the trap. When a sufficient weight of water had been expelled, the counterbalance raised the chamber, which closed the valve and completed the cycle. *Photo by Charles W. Chesterman.*



# CEMENT

By OLIVER E. BOWEN, JR.

Production of portland cement has become one of the state's foremost mineral industries. The value of cement produced in California in 1955 reached \$103,793,702 and now is second only to the value of California petroleum products. The cement plants are grouped around the two principal marketing areas—Los Angeles and San Francisco—and lie within a radius of 125 miles of one or the other of these centers. Most of the mineral material consumed by these plants is obtained close to them, and all but an insignificant proportion of raw materials consumed are obtained from sources in California. The supply of California raw materials suitable for portland cement is nearly inexhaustible, but some deposits are less conveniently situated than those now being exploited.

*The Nature of Portland Cement.* Portland cement is the chief binding agent used in modern concrete and is also an important constituent of mortars and plasters used by the construction industry. Its most useful characteristic is the ability to set into a stable binder in the presence of water. Portland cement is manufactured by calcining and heating to incipient fusion, under carefully controlled conditions, suitable mixtures of finely ground raw materials that include as essential ingredients calcium carbonate ( $\text{CaCO}_3$ ), silica ( $\text{SiO}_2$ ), and alumina ( $\text{Al}_2\text{O}_3$ ). Iron oxide is also an important constituent in several types of cement, particularly the sulfate-resistant types. With the exception of white cement, in which the iron content is kept well under one percent, portland cements generally contain some iron oxide ( $\text{Fe}_2\text{O}_3$ ). Blended portland cement mixtures ready to be fed into the kilns generally lie within the following chemical limits (dry basis).

Lime ( $\text{CaO}$ )	42-44%
Silica ( $\text{SiO}_2$ )	13-15%
Alumina ( $\text{Al}_2\text{O}_3$ )	4-6%
Iron oxide ( $\text{Fe}_2\text{O}_3$ )	2-3%
Carbon dioxide ( $\text{CO}_2$ )	33-35%
Remainder	less than 1-3%
[includes magnesia ( $\text{MgO}$ ), and alkalis such as potash ( $\text{K}_2\text{O}$ ) and soda ( $\text{Na}_2\text{O}$ )].	

The degree of variance within these ranges depends upon the type of cement being produced and the available raw materials.

During the burning operation the pulverized raw materials are converted into clinkery particles called clinker, composed of new, anhydrous, lime-bearing compounds with loss of a large volume of carbon dioxide—about 35 percent of the raw mix (dry basis). A typical Type I clinker has the following analysis:

Silica ( $\text{SiO}_2$ )	21.3%
Alumina ( $\text{Al}_2\text{O}_3$ )	6.0%
Iron oxide ( $\text{Fe}_2\text{O}_3$ )	2.7%
Lime ( $\text{CaO}$ )	63.2%
Magnesia ( $\text{MgO}$ )	2.0%
Sulfur trioxide ( $\text{SO}_3$ )	1.8%
Ignition loss	1.3%
Insolubles	0.2%
Total	98.5%

Portland cement is made by grinding the clinker to a very fine powder. A small amount of gypsum, about 11 pounds per barrel, is interground with the clinker to control the setting time. The ground portland cement

clinker readily combines with water to form new, stable crystals. Concrete is simply a mass of rock particles of various sizes bound together by crisscrossed, interlocking, hydrous crystals that form as the cement sets.

Although some of the reactions that take place during the burning operation, and also during the hydration of portland cement, are imperfectly known, it is generally believed that the chief binding compounds are: tricalcium silicate ( $3\text{CaO}\cdot\text{SiO}_2$ ), dicalcium silicate ( $2\text{CaO}\cdot\text{SiO}_2$ ), tricalcium aluminate ( $3\text{CaO}\cdot\text{Al}_2\text{O}_3$ ) and tetracalcium aluminoferrite ( $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{Fe}_2\text{O}_3$ ). Each of these has a distinctive behavior or set of characteristics during hydration or setting. By controlling the raw material mix and the time and temperature of calcination and clinkering, various combinations of these compounds can be obtained in the clinker and several types of cement can be produced. Each type is designed for a specific use.

The American Society for Testing Materials has, since 1940, recognized five types of portland cement having the following general uses (see A. S. T. M. C. 150-53):

Type I—for general use in concrete construction where special properties specified for types II-V are not required.

Type II—for use in general concrete construction where moderate sulfate action is anticipated or where moderate heat of hydration is desired.

Type III—for use where high early-strength is required.

Type IV—for use where low heat of hydration is required.

Type V—for use where high sulfate resistance is required.

White portland cement is a variety of Type I cement in which iron is kept at a minimum—preferably less than 0.5 percent as ferric oxide. White cement of present manufacturers varies from 0.25 to 0.5 percent ferric oxide in the finished product. In addition to the limitation on iron, manganese and titanium may not be present in white cement in greater than trace amounts as manganese tends to color cement green and titanium colors it yellow.

Dicalcium and tricalcium silicates are the principal components in portland cement and form 70-80 percent of the finished product. They are the chief strength-producing compounds. Tricalcium silicate hydrates rapidly and yields high strength in concrete in early stages of setting. Dicalcium silicate hydrates more slowly and contributes strength to concrete later in the hardening process. Type III or high-early-strength cement, therefore, contains a higher percentage of tricalcium silicate than other types. In addition it is ground finer, as fine-grinding accelerates the hydration and consequently the strength in early stages of setting.

Both tricalcium silicate and tricalcium aluminate liberate a considerable amount of heat during hydration. In massive concrete structures such as dams the heat liberated during hydration cannot readily escape from the interior and hence raises the temperature of the con-





FIGURE 1. Aerial oblique view of the Permanente Cement Company plant near Los Altos, Santa Clara County. Observer facing northwest. Built in 1942 and enlarged on several occasions, this plant now has an annual capacity of 8,400,000 barrels or 33,600,000 sacks of cement, making it the largest plant in the western United States. *Photo courtesy Kaiser Services, Graphic Arts Department.*

crete. Marked temperature differences between the interior and exterior of such structures can cause failure by cracking. Consequently, the Type IV portland cements which are used for such structures are designed to liberate as little heat as possible. In these cements the tricalcium silicate is limited and the dicalcium silicate increased proportionately. Tricalcium aluminate is strictly limited and the tetracalcium aluminoferrite content, which liberates much less heat during hydration than the other cementitious compounds, is somewhat increased.

Concrete made from ordinary or Type I portland cement usually expands and cracks when in contact with strong sulfate-bearing water. Such deterioration is largely an effect of the reaction between tricalcium aluminate and the sulfate water. This reaction yields calcium-sulfo-aluminates which have greater volume

than the original tricalcium aluminate. Type V cement, which is low in tricalcium aluminate, is used in construction where strong sulfate reactivity is probable and Type II cement is used where moderate sulfate reactivity is probable.

In recent years much attention has been paid to harmful reactions between unsuitable aggregate materials and portland cement in concrete. These reactions are not the result of any fundamental weakness in the quality of portland cement, which is made under very rigid specifications and carefully controlled conditions, but rather are caused by the poor quality aggregate which must be utilized in some areas. The reactions, which may take place years after the concrete has set and hardened, result in formation of new chemical compounds which require greater space than that present in voids between the aggregate particles. Cracks, popouts (spalling) and



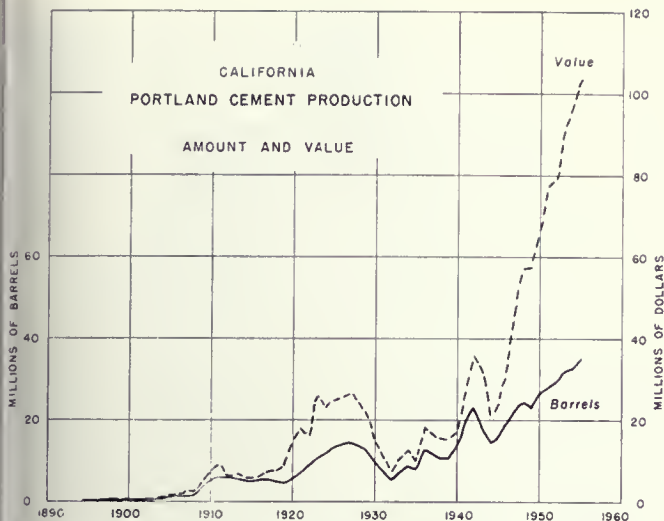


FIGURE 2. Chart showing the amount and value of portland cement produced in California from 1894 to 1955.

other damage to the concrete result. To combat such failures cement companies have developed special cements for use with poor quality aggregate. Extensive research has revealed that numerous failures have been caused by reactions between small amounts of contaminating alkalis, chiefly potash ( $K_2O$ ) and soda ( $Na_2O$ ) and minerals present in the aggregate (such as opal, nontronite and zeolites). These alkali contaminants, which are not essential to any of the desirable reactions taking place during setting of concrete, commonly are present in small amounts in cement raw materials. Consequently, the alkali content of both cement and the raw materials from which it is made is very carefully controlled, and low-alkali cements are specified for use on projects where alkali-aggregate reactivity may be a factor. Low-alkali cements are designated as those having less than 0.60 percent of total alkalis expressed as  $Na_2O$  in the finished product. Crystalline magnesia, or periclase, sometimes causes a delayed abnormal expansion and cracking in concrete. The magnesium oxide content of the finished cement must be held to not more than 5 percent in Types I to IV and not more than 4 percent in Type V. Most cement chemists keep their cement well below the 5 percent limit.

Pozzolanic additives for use with portland cement in concrete have been developed partly to avoid the harmful effects of alkali-aggregates reaction and to improve the strength and general appearance of concrete. Pozzolans are satisfactory low-cost partial substitutes for portland cement if high early strength is not required in the concrete; they latently increase the strength and textural quality of concrete over a period of time as long as two or three years; and, most significantly, they are effective in combining with alkalis to form compounds that are not injurious to concrete. Although the reactions taking place during setting of a pozzolanic portland cement are not fully known, it is believed that opaline silica is the chief active ingredient. Pulverized pozzolanic additives are introduced into the concrete mix; they commonly are not mixed with cement before it is marketed. Opaline chert and shale, acid volcanic tuffs, burned diatomaceous shale and even residual tufa have been utilized success-

fully for pozzolans in California. Pozzolans usually are tested in concrete before being used on large projects.

Air entrainment is another relatively new development in portland cement technology. Although considerable air is normally trapped in concrete during the mixing process, more can be introduced and uniformly distributed by use of synthetic additives such as certain resins and hydrous silicates of calcium. Air-entrained concrete has superior frost and weathering resistance, increased workability and cohesiveness, reduced tendencies toward segregation and bleeding (separation of water and cementitious particles), reduced weight and permeability, and increased resistance to deterioration by sulfate water. The increased porosity and decreased permeability are caused by the large number of unconnected, nearly spherical voids induced by the air entrainment additives. Increased resistance to frost action, decreased weight and decreased thermal conductivity are the chief advantages of air-entrained concrete over common concrete. These advantages are sometimes achieved at only a slight loss in strength of the concrete.

Several kinds of cement are designed to have special characteristics, such as waterproof, plastic and numerous oil well varieties. Waterproof and plastic cements are portland cement mixed with various preparations which produce or enhance the desired special characteristics. Oil well cements, which must set under a variety of conditions of temperature, pressure, and water quality, commonly are manufactured under more rigid specifications.

The content of cementitious compounds is closely controlled and many oil well cements contain special additives that control such factors as the speed of set and permeability of the set cement. Special mixing procedures have also been devised for oil well cements. A detailed discussion of oil well cements may be found on pages 488-505 of *Petroleum Production Engineering* by L. C. Uren (McGraw-Hill Book Co., 1946).

*Nature and Geologic Occurrence of California Raw Materials Used in Cement.* High-calcium limestone is the most common source of calcium carbonate used in cement, and some form of clay is the commonest source of alumina and silica. However, a wide variety of satisfactory substitute materials is utilized because such material can be more easily obtained at low cost than more ideal ingredients. In some parts of the United States natural rocks occur that already contain the essential components for making portland cement in approximately the desired proportions. Such rocks, known as cement rocks, most commonly are marine argillaceous (clayey) limestones. To date no large cement-rock deposits have been discovered in California that are near enough to marketing centers to be utilized. Various types of limestone and sea shells supply nearly all of the calcium carbonate used in the cement manufactured in California.

With one exception, the limestones quarried in California for portland cement are coarsely crystalline metamorphic rocks of Paleozoic or Jurassic-Triassic age. The Permanente cement plant in Santa Clara County utilizes a dense, fine-grained limestone of late Mesozoic age. Limestones suitable for cement are widely distributed in California from Siskiyou and Shasta Counties south through the Sierra Nevada into southern California.





FIGURE 3. Front view, observer facing west, of one of the first cement kilns built in California. The structure stands on the Jamul (G. R. Dailey) Ranch near Jamul, San Diego County. Completed in 1891, it is believed to be the second oldest installation in California that produced cement approaching the characteristics of portland cement. The oldest kiln, no longer in a good state of preservation, was built at Santa Cruz in 1877. A natural hydraulic cement was made at Benicia, Solano County, as early as 1859. The building is roughly 36 feet square and 15 feet thick, exclusive of the stack and uppermost arches. The stack extends 30 feet above the main part of the structure.

They are broadly distributed throughout the Mojave Desert and Basin Ranges provinces and through the northern part of the Transverse and eastern part of the Peninsular Ranges of southern California. Large deposits are much more sparsely distributed in the Coast Ranges, being found chiefly in Santa Cruz County. Sea shells and bay mud are the sole raw materials utilized by one plant on San Francisco Bay. Similar materials are found in Newport and San Diego Bays in southern California.

Many California limestones contain an appreciable amount of magnesium, which is the only serious detrimental ingredient commonly found in limestone that is used for cement. As the magnesium oxide content of portland cement clinker must be kept below 5 percent, most cement plants will not use limestone which, in crude form, averages more than 3 percent  $MgO$ . As the magnesium content may vary considerably within a given deposit, close sampling and testing are necessary both before and during quarrying.

Alluvial and residual clays, clay shale and quartz-mica schist derived from clay shale are the commonest sources of alumina and silica used in California. Quartzite, high alumina laterite, quartz diorite and partly altered volcanic rocks are used at some plants in lieu of more suitable material because they are readily available or supply a particular need. Alluvium (e.g. mixed de-

posits of clay, sand and gravel) commonly is utilized. Magnesia and alkalis (soda and potash) are the critical impurities that must be kept at a minimum in the siliceous and aluminous fractions used in cement. Both magnesia and total alkalis are generally kept below 1 percent in the siliceous and aluminous raw materials.

Although most clays and clay shales contain some iron, iron commonly is added in manufacture of some types of cement. Pyrite cinder, the black-to-red residue resulting from manufacture of sulfuric acid from pyrite, is the most widely used source of iron in California cement plants. Southern California plants use a considerable tonnage of hematite-magnetite ores from San Bernardino and Riverside Counties.

Gypsum, an essential additive in all types of portland cement, regulates the initial setting of cement in concrete. From 2 to 5 percent of gypsum is introduced into the finish-grinding circuit either as rock gypsum, in lump form, or as by-product gypsum in semipulverized form. The by-product gypsum, which comprises a relatively small percentage of the annual consumption of gypsum by California cement mills, is supplied by chemical plants. A substantial proportion of gypsum is supplied by deposits in Ventura, Riverside and Imperial Counties, but considerable gypsum is imported from western Nevada and from San Marcos Island in the Gulf of California. Deposits in California could supply all of the requirements of the cement plants, but much of their production is diverted to other uses.

Fluorspar (calcium fluoride,  $CaF_2$ ) is sometimes added to portland cement raw mixes in proportions up to 1 percent to facilitate the calcination process and



FIGURE 4. Side view, observer facing south, of the same structure shown in figure 3. The hills in the background are underlain by massive metavolcanic rocks, schistose metasediments, and granitic rocks. Most of these rock types may be found making up the masonry structure.





FIGURE 5. A closer view of the Jamul cement kiln. The massive part of the structure consists of partially shaped blocks of field stone laid up in mortar. The stone is predominantly a hard, dark-colored metabasalt not easily shaped into blocks. The stack and uppermost arches of the kiln consist of common red brick laid up in mortar whereas the kiln and flue linings are English fire-brick. The state of preservation is excellent.

improve certain characteristics of the cement. Calcium fluoride tends to reduce the uncombined lime ( $\text{CaO}$ ) in clinker and lowers the clinkering temperature (in some cases as much as  $200^{\circ}\text{C}.$ ). There is no current production of fluorite in California, and as it must be brought in at considerable expense and as there is possible risk of air pollution from its use, consumption of fluorite by the California cement industry is negligible.

Calcium chloride is another chemical which may be added to portland cement to control the speed of hydration and to induce high early strength in concrete. It most commonly is added to Type I cement. Calcium chloride, in quantity, is produced from brine by several California chemical plants.

During 1955, California cement mills consumed 12,236,471 short tons of materials according to the following table:

	Northern California mills	Southern California mills	State total
Limestone, oyster shells, cement rocks -----	4,770,586	5,692,148	10,462,734
Aluminous and * siliceous rocks -----	590,669	819,930	1,410,599
Iron ore, pyrite cinder and mill scale -----	26,975	60,730	87,705
Gypsum -----	122,933	151,648	274,581
Miscellaneous * -----	760	92	852

\* Includes alluvium, clay, clay shale, tufa, mica schist, quartz, sandstone, diorite, quartzite, and altered volcanic rocks.

\*\* Includes fluorspar, air-entraining compounds, calcium chloride, grinding aids and tuff pozzolan.

**Mining and Manufacturing Methods.** Most of the raw materials used in portland cement are mined by

open-pit methods, but two California operations employ underground mining. Clays and clay shales commonly can be removed without blasting, but most California limestones must be broken with explosives. Blast holes now are drilled principally with rotary drills instead of the percussion type drills formerly employed. Materials are transported from quarry to plant by trucks, railroads, belt conveyors or by various combinations of these. Specially designed rear- and side-dump trucks, trailers and railroad cars are constantly being devised to better accomplish particular hauling jobs under special conditions. Primary crushing is sometimes done at the quarry and sometimes at the plant; secondary crushing is almost always done at the plant. Jaw, gyratory and cone crushers are all utilized in various primary crushing circuits; ball mills, tube mills or rod mills generally are utilized for grinding. Sizes to which raw materials are crushed during the various stages of crushing and grinding depend to a considerable extent upon the types of processing equipment employed. Material fed to the kilns is generally controlled to around 90 percent minus-200 mesh.

Two general processes are employed in California cement plants—the wet process and the dry. In the wet process the ground materials are made into a water slurry during the grinding process before burning; whereas in the dry process materials are ground dry and no water is added during the manufacturing process unless nodulizing is employed. Each process has its own advantages and disadvantages depending upon local economic conditions. The wet process has advan-



FIGURE 6. Detail of the archways in the Jamul kilns. The light-colored fire-brick flue lining stands out from the darker-colored common brick. Arches are partly supported by cast mortar or concrete. The interior of the kilns and the inner surface of the flues is lined with about a quarter of an inch of vitreous matter formed during burning of the cement. Charcoal, prepared from local vegetation, was used for fuel.



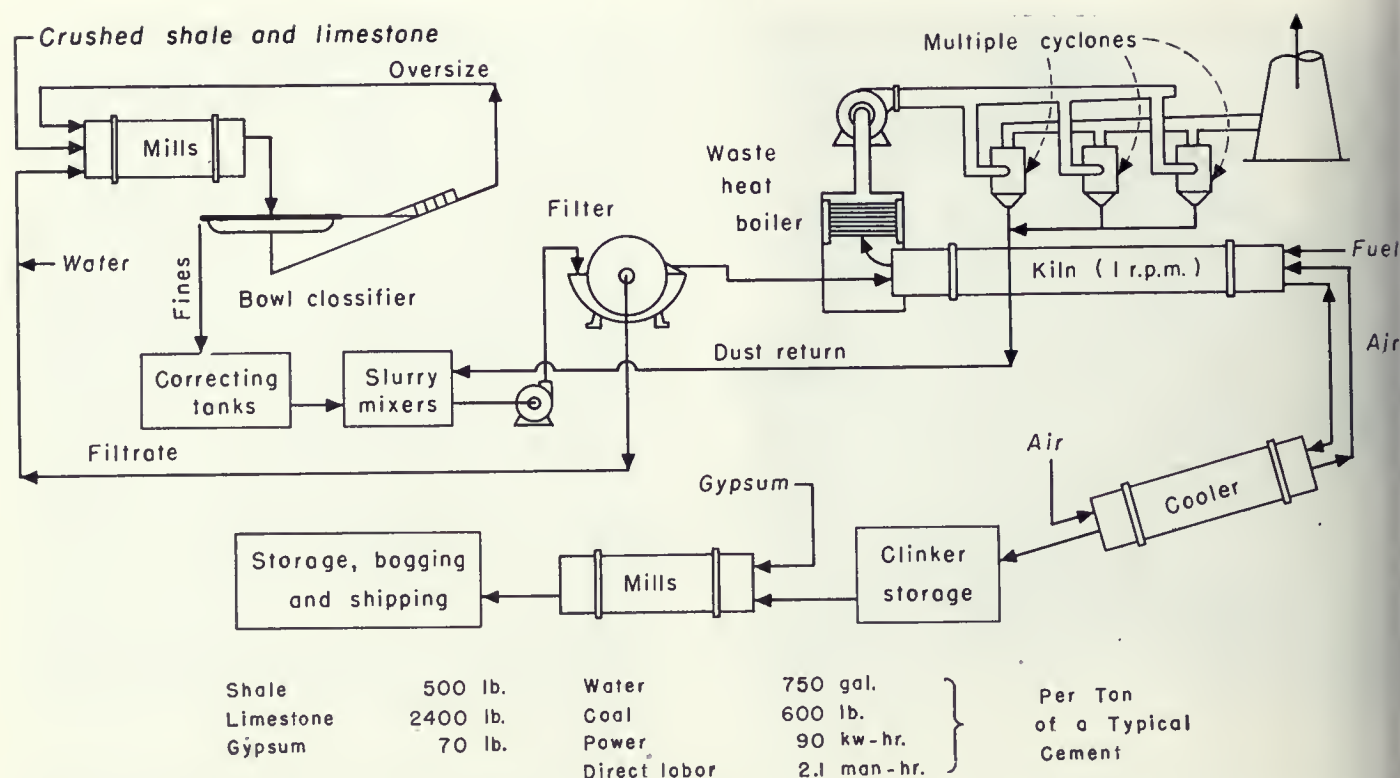


FIGURE 7. Flow sheet of a typical wet process portland cement plant showing materials, power, water, and labor consumed per ton of cement manufactured. In western states, oil or gas is used for fuel instead of coal. *Diagram courtesy Chemistry and Metallurgy.*

tages in ease of mixing and transportation of slurry and in plant cleanliness, but the water must be driven off at considerable expense during calcining.

In both processes the ground raw materials are stored for blending in large silos prior to being fired to clinker. The chemical composition of the raw mix is very carefully checked at this stage. Raw materials blended from various silos to close tolerances are then fed into large rotary kilns and fired at temperatures within the range of 2600° F. to 2900° F. Optimum temperature depends upon the type of cement being made. In some dry-process plants the blended raw materials are nodulized before entering the kiln to improve uniformity of burning. The clinker is then cooled, blended with gypsum, ground and stored in silos for bulk or sack shipment. At present more than 85 percent of the cement sold is delivered in bulk.

**Centers of Production.** The cement production and distribution centers in California are: the Colton-Riverside district, Riverside and San Bernardino Counties; the Victorville-Oro Grande-Lucerne Valley district, San Bernardino County; the Monolith-Mojave-Willow Springs district of Kern County; San Andreas, Calaveras County; San Juan Bautista, San Benito County; Davenport-Santa Cruz district, Santa Cruz County; Permanente, Santa Clara County, and Redwood City, San Mateo County. Most raw material deposits are situated close to the processing plants. Between 1940 and 1954 the increased demand for cement in California was satisfied by enlarging existing plants and streamlining existing production facilities. All of the operating companies have made large expenditures in new kilns and support-

ing equipment and in prolonged raw material exploration and development programs. Between 1954 and 1956, however, two new plants were constructed, one near Mojave, Kern County, and one near Lucerne Valley, San Bernardino County. Several companies that heretofore have not operated in California have been looking into possibilities of new construction in California, and it is believed that other new plants will ultimately be built.

Localities which appear most favorable for future development are those within or close to a 125-mile radius of Los Angeles, San Francisco and San Diego. San Diego has grown so in recent years that the marketing potential is rapidly becoming attractive to a new cement operator. The Dos Cabezas district of eastern San Diego County and the Coyote Mountains of western Imperial County appear to have the only resources of raw materials sufficiently large to support a cement plant of average size near to the San Diego market and north of the Mexican border.

Among the larger deposits that are sufficiently well situated to be considered as potential immediate sources of cement raw materials for the Los Angeles market are those within the Beaumont-San Jacinto-Palm Springs triangle of the San Jacinto Mountains. Proposed plants in this vicinity have, however, met with formidable opposition from other interests because of the fear of dust, smog and noise. Location of acceptable sites near to the marketing centers is becoming increasingly difficult as the population increases.

A series of small deposits in the Wrightwood-Lone Pine Canyon district in the San Gabriel Mountains near the border common to Los Angeles and San Bernardino Counties may contain an aggregate tonnage sufficiently



large to support a cement plant. It is doubtful, however, if any one of these is large enough. The district has not been thoroughly explored.

As deposits in the Victorville-Oro Grande district are gradually depleted, limestone production for cement will probably fan out into adjacent parts of the Mojave Desert. Reserves in this district, however, run into many hundreds of millions of tons so that further moves there are unlikely in the near future. The same situation exists in the adjacent Lucerne Valley-Cushenbury Canyon district.

In northern California, extensive undeveloped deposits of raw materials are found in the Sierran foothills, notably in the Sonora-Columbia area of northern Tuolumne County, Volcano, Amador County, and the Three Rivers District of Tulare County.

Probably the largest readily accessible, uniform limestone deposits in California are found in Shasta County north and northeast of Redding. Although the Shasta County deposits are far outside the San Francisco marketing perimeter, promulgation of several large public works programs that have been proposed for this area might attract the cement industry farther away from present marketing centers.

*History of the Cement Industry in California.* Between 1859 and 1891 there was a small intermittent production of natural hydraulic cement in California, chiefly from the Benicia Cement Company at Benicia, now in Solano County. In 1859 and 1860 this company was producing 50 to 100 barrels per day at a mill price of \$4.00 per barrel. At that time it was estimated that San Francisco was using 12,000 barrels a year (Mercantile Trust Company Review, 1925). By 1865, the San Francisco rate of consumption had increased to 100,000 barrels annually and the price of hydraulic cement had fallen to \$2.50 per barrel. Most of the cement consumed in California prior to 1877 was imported from England.

Because of the incomplete reporting of mineral statistics prior to 1894, there has been some confusion as to where the first portland-type cement was produced in California. Some recent data collected by R. A. Kinzie, Jr. of Santa Cruz Portland Cement Company shows that a corporation known as California Portland Cement Company was organized January 13, 1877 at Santa Cruz. This firm, not the same as the present-day California Portland Cement Corporation, apparently remained in business only a short time, but the name was retained on corporation lists as late as the mid-1920s. Cement was manufactured in stationary kilns constructed of brick. Limestone for the cement came from the vicinity of present-day Wagner Park and clay was taken from pits at the head of Walnut Avenue in Santa Cruz. Prior to the time this information was made known, the plant erected on the Jamul Ranch, San Diego County in 1891 was credited as being the first portland cement plant in California (Storms 1892).

During that year a plant with a daily capacity of 150 barrels was put into operation by the Jamul Portland Cement Works. This operation lasted less than a year. Because of competition from low-cost cements shipped by water from England and other European countries, production of portland cement increased very slowly through the 1890s. An increase from 5,000 to 52,000 barrels per year was recorded during that period. Between

1902 and the pre-World War I slump of 1912-16, production increased from 171,000 to 6,371,369 barrels. A new high of over 35,000,000 barrels was recorded during 1955. Salient events in the California cement industry are as follows:

- 1860—First California production of natural cement at Benicia, Solano County. Cement was produced intermittently at Benicia until 1890.
- 1877—Erection of the first California plant for production of portland cement at Santa Cruz, Santa Cruz County, by a firm known as California Portland Cement Company (not the same as the firm currently active in southern California).
- 1891—Erection of a cement plant at Jamul Ranch, San Diego County. Production there ceased in 1892 owing to high transportation costs and competition with foreign cement. (The Jamul product was classified by some as a natural cement.)
- 1894—Opening of the first cement plant in California to survive up to the present day, that of California Portland Cement Company at Colton, San Bernardino County.
- 1902-3 Establishment of two plants, one near Napa, Napa County by Standard Portland Cement Company and one at Cement, near Fairfield, Solano County, by Pacific Portland Cement Company. The Napa plant closed in 1919 and the Fairfield plant in 1927, both because raw materials were exhausted.
- 1906—Opening of the plant at Davenport, Santa Cruz County, by Standard Portland Cement Company. This plant is now operated by Santa Cruz Portland Cement Company.
- 1908—First shipments of cement made from Henry Cowell Lime and Cement Company at Cowell, Contra Costa County. Depletion of raw material deposits and loss of rail facilities resulted in closing of plant in 1942.
- 1909—Plant of Riverside Portland Cement Company erected at Crestmore, Riverside County; also, a plant at Monolith, Kern County, was built by the City of Los Angeles. This plant, built to supply cement for the L. A. aqueduct, is now operated by Monolith Portland Cement Co.
- 1910—The Golden State Portland Cement Company commenced production at Oro Grande, San Bernardino County. Plant was later taken over by Riverside Cement Company and recently was rebuilt.
- 1914—Erection of Old Mission Portland Cement Company plant at San Juan Bautista, San Benito County. Plant, which later passed into hands of Pacific Portland Cement Company, began shipping cement in 1918. It is now operated by Ideal Cement Company.
- 1916—Establishment of plant of Southwestern Portland Cement Company at Victorville, San Bernardino County. This plant recently has been modernized and enlarged.
- 1924—Opening of Pacific Portland Cement Company plant at Redwood City, San Mateo County. This plant is now operated by Ideal Cement Company.



- 1925—Yosemite Portland Cement Company plant built at Merced, Merced County. Plant was closed down in June 30, 1944 when traffic over Yosemite Valley Railroad was discontinued.
- 1926—Calaveras Cement Company plant opened at San Andreas, Calaveras County. This plant has been tripled in size since World War II.
- 1930—Blue Diamond Corporation, Ltd. completed a grinding and finishing plant at Los Angeles utilizing cement clinker purchased from other companies. The plant is still in use.
- 1931—National Cement Company of Dallas, Texas, built a small plant (annual capacity 5,320 bbls.) for making white portland cement at Chubbuck, San Bernardino County. This plant never operated at full capacity and was shut down in 1932.
- 1940—Establishment of Permanente Cement Company plant at Permanente, Santa Clara County, currently the largest cement producer in California.
- 1952—Ideal Cement Company acquired the holdings of Pacific Portland Cement Company.
- 1954—California Portland Cement Company began construction of a new cement plant at Creal, near Mojave, Kern County.
- 1955—Permanente Cement Company began construction of a second plant near Lucerne Valley, San Bernardino County.

*Utilization and Markets.* From the beginning of the portland cement industry in California all but a small part of the cement produced has been marketed and used in this state. Less than 15 percent, and in some years less than 10 percent, of the production has been shipped out of the state. Most of this has been consumed in the Pacific islands and Latin America. High transportation costs prevent California from competing consistently with plants in other Pacific Coast states.

As portland cement is primarily a construction material, increases in production and markets have been governed largely by building booms, large public works projects, and wartime expansion of industrial and military facilities. The unprecedented postwar house construction boom in California, the expanded road-building program and vastly increased oil exploration have all contributed to the demand for cement.

As it is a relatively low-cost product with a small margin of profit, cement must be produced as close to centers of population as the availability of raw materials will permit. Five cement plants are located within a radius of 125 miles of San Francisco and seven within a similar distance of Los Angeles. An eighth is in process of construction within 125 miles of Los Angeles, near Lucerne Valley, San Bernardino County. Although future plants may be built outside of the 125-mile zone of the two large marketing areas, the utilization of processes designed to improve the grade of less suitable raw materials situated within that perimeter may prevent it. A possible exception would be development of Shasta County deposits for cement in the event of commencement of several large public works projects such as the proposed Trinity and Feather River dams.

The average mill price paid for portland cement produced at California plants during 1955 was \$2.96 per barrel of 376 pounds. This is 10 cents per barrel higher

than the average national figure of \$2.86, as might be expected in an area of peak demand. In other years, however, the cost of California cement has been materially less than the national average.

Typical price differentials among the various types of portland cement may be seen in the following table of U. S. Bureau of Mines figures for California for 1955. Average prices obtained for cement packaged in 94-pound paper bags during 1955 were:

Type of cement	Average price per barrel
I and II—General use and moderate heat	\$2.93
III—High early strength	3.83
IV—Low heat	4.02
V—Sulfate resistant	3.47
Oil well	3.26
White	8.14
Portland—pozzolan	2.99
Air-entrained	2.75
Waterproofed	3.50
Miscellaneous	3.42
Average	2.96

Cement sold in bags generally averages 40 cents per barrel higher than the bulk price. More than 85 percent of the cement sold in California is marketed in bulk; 15 percent or less is packaged. Northern California mills charge a premium of 20 cents per barrel on Type II cement.

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# CHROMITE

BY SALEM J. RICE

Chromite is the only ore mineral of chromium, an essential ingredient in the manufacture of a great variety of steels. In addition, it is the basic raw material in the production of numerous chemicals and in the manufacture of special refractory materials. Thus it is not only a strategic mineral essential to the defense program of the United States, but it is also a raw material of considerable importance to our peacetime industrial economy.

The chromite produced in the U. S. has always fallen far short of supplying domestic requirements. These have been met by imports, principally from Turkey, Africa, the Philippines, New Caledonia, and Cuba. During 1955, for example, 1,583,983 short tons of chromite was consumed in the U. S., while domestic production was only 153,225 short tons. All of the latter went to the national stockpile at incentive prices considerably higher than those of the open market. Although chromite was reported produced in the U. S. as early as 1827, the entire domestic output through 1955 was only about 1,252,000 short tons, which is equivalent to less than 10 months' supply at the 1955 rate of consumption.

Chromite production was first recorded in California in 1869. From then through 1955 an estimated 534,000 short tons valued at approximately \$20,800,000 had been produced in the state (fig. 1). Almost two-thirds of this output was mined during World Wars I and II, when foreign sources of supply were virtually cut off. Much of the remainder was mined during the period 1869-95,

prior to the development of many of the foreign deposits which now contribute most of the world production.

California is richly endowed with serpentine and peridotite, the host rocks of chromite deposits, and over 1,200 known deposits are widely distributed in the Coast Ranges, Klamath Mountains, and foothills of the Sierra Nevada. Although California chromite miners have not been able to compete successfully with foreign sources during normal times, our deposits constitute a valuable reserve that can be mined if prices permit.

**Mineralogy and Geologic Occurrence.** Chromite, a heavy black mineral with a submetallic luster, is a member of the spinel group of isometric minerals. Most of the physical properties of chromite vary with the composition of the mineral. It has a specific gravity between 4.5 and 4.8, and the melting point ranges from 1545° C to 1730° C. As its hardness is about 5 (Mohs' scale) it is scratched readily with a knife. Chromite is most easily distinguished from other similar-appearing minerals by its brown streak, or powder, and by its mode of occurrence. The streak and a much smaller magnetic susceptibility distinguish it from magnetite, a mineral of similar color, luster, and specific gravity, which commonly is associated with chromite. Chromite has a theoretical formula of  $\text{FeCr}_2\text{O}_4$ . However, it ordinarily consists of various proportions of an isomorphous series of oxides of chromium, magnesium, iron, and aluminum, as shown by the representative analyses in table 1. Thus the chemical formula is more accurately written  $(\text{Fe,Mg})\text{O} \cdot (\text{Cr,Al,Fe})_2\text{O}_3$  (Stephens, 1944).

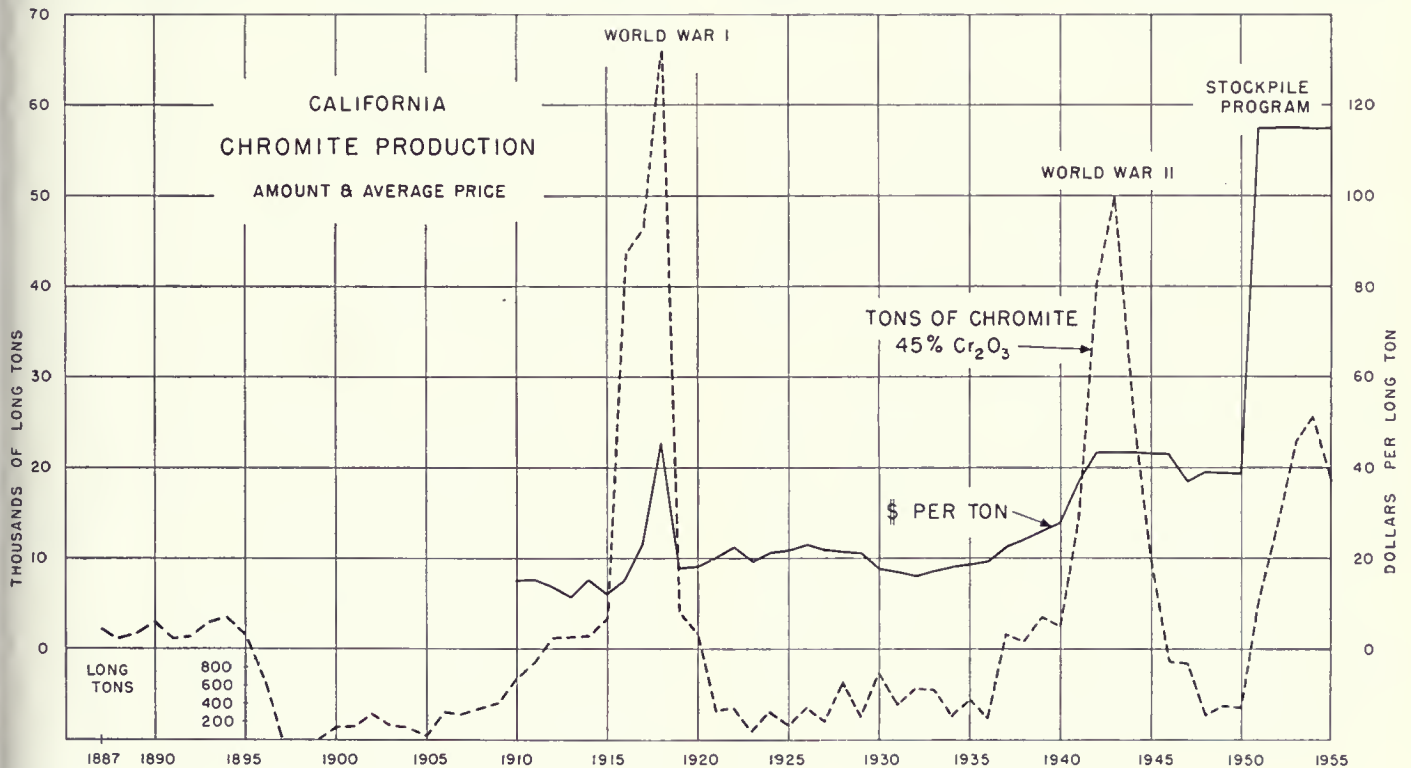


FIGURE 1.



Table 1. Analyses of chromite indicating range in composition.

	(1)	(2)	(3)	(4)	(5)
Cr <sub>2</sub> O <sub>3</sub> -----	58.45	52.77	47.57	41.78	35.4
Al <sub>2</sub> O <sub>3</sub> -----	9.36	10.31	18.61	26.70	28.3
FeO-----	4.47	9.99	4.80	3.16	5.5
FeO-----	14.15	12.40	13.06	11.33	13.6
MgO-----	12.71	12.10	13.91	16.15	15.3
MnO-----	0.12	0.32	0.14	0.11	0.1
CaO-----	none	0.16	0.24	0.14	0.1
TiO <sub>2</sub> -----	0.33	0.17	0.13	0.31	0.3
SiO <sub>2</sub> -----	0.22	0.92	0.86	0.68	0.3
H <sub>2</sub> O+-----	0.08	0.76	0.54	trace	0.4
	99.89	99.90	99.86	100.36	99.3

(1) Veta Chica deposit, Siskiyou County, California (Stevens, 1944, sample no. 15).

(2) Pilliken mine, El Dorado County, California (Stevens, 1944, sample no. 6).

(3) Castro mine, San Luis Obispo County, California (Stevens, 1944, sample no. 12).

(4) Clemencia mine, Holguin district, Cuba (Stevens, 1944, sample no. 41).

(5) Chambers mine, Grant County, Oregon (Stevens, 1944, sample no. 22).

Several secondary chromium-bearing minerals of no commercial importance occur in many California chromite deposits as veinlets, stains, or incrustations in or on the ore. The most common of these are uvarovite, an emerald-green garnet, and kammererite, a pink to purple variety of chlorite.

All primary deposits of chromite occur in ultrabasic igneous rocks, such as peridotite and dunite, or in serpentine derived from such rocks. Peridotite is an igneous rock composed predominantly of silicate minerals rich in magnesium and iron, particularly olivine and some pyroxenes. Peridotite can be subdivided into several varietal types, largely depending upon the relative percentages of the minerals present. Thus saxonite is a variety composed largely of olivine and the pyroxene enstatite, dunite contains over 95 percent of olivine, and pyroxenite consists of more than 95 percent of pyroxene. Chromite grains generally are sparsely disseminated throughout these rocks as a minor constituent, but locally are abundant enough to form ore bodies.

Saxonite is by far the most abundant variety of peridotite in California, but dunite is common, particularly as masses enclosed in saxonite. Most pyroxenite bodies occur as veins or dikes cutting saxonite. Most commercial deposits of chromite are found in dunite, although the latter may only form a thin rind enclosing the ore.

Because olivine and pyroxene are readily altered to serpentine minerals, most masses of peridotite are altered partially or entirely to serpentine. Chromite apparently is not affected by this alteration process; thus chromite concentrations originally present in the peridotite will remain in the resulting serpentine. However, in the process of serpentinization the iron in the olivine is oxidized to form magnetite, which is difficult to separate in the treatment of chromite ores.

Two types of chromite ore are found in primary deposits. One contains grains, nodules, stringers, or thin layers of chromite dispersed in the host rock, and is called disseminated ore. The other consists of masses of chromite containing little or no interstitial silicate minerals and large enough to be mined as massive ore. Disseminated ore must be milled and concentrated before it can be marketed, but massive ore can ordinarily be sold in lump form without mechanical concentration.

Chromite ore bodies occur in a variety of forms. Most have a roughly tabular or lenticular shape, but many massive ore bodies have irregular shapes and are locally given such descriptive designations as pods, kidneys, knockers, chimneys, and stringers. Some deposits consist of layers of massive and disseminated ore alternating with layers of barren rock, thus having a stratified appearance (fig. 2). Although layered deposits are relatively rare in California, foreign deposits of this type comprise much of the potential chromite reserves of the world.

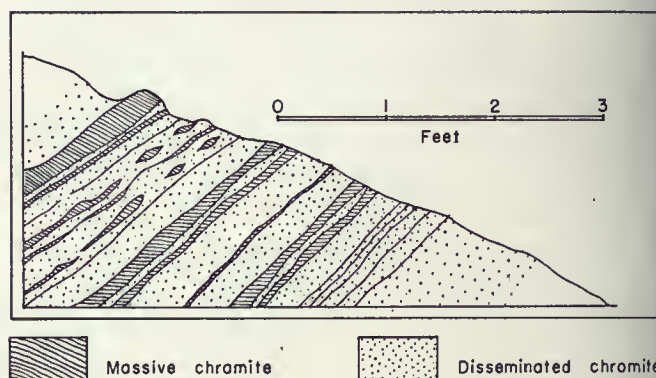


FIGURE 2. Cross section of ore body, Black Eagle claim north of Seiad, Siskiyou County California. (From Allen, 1941.)

Although most chromite bodies contain less than 100 tons of ore, many foreign deposits have yielded more than 100,000 tons. For example, the Tiebaghi mine in New Caledonia has yielded about 1,500,000 tons of high grade massive ore averaging 55 to 57 percent Cr<sub>2</sub>O<sub>3</sub> (Maxwell, 1949). The Guleman mine, in Turkey, consists of many large ore bodies of massive chromite in a narrow mass of serpentine. Information is not available regarding the exact size of the individual ore bodies, which are vertical pipe-like masses, but the outcrop area of the largest is about 40,000 square feet. In 1939 the fully developed ore reserves of the Guleman mine were about 750,000 tons. Most of the ore contains more than 50 percent Cr<sub>2</sub>O<sub>3</sub> (Perkins, 1939). The deposits of chromite in Southern Rhodesia and the Transvaal are also very large.

Most, if not all, primary chromite deposits originated as magmatic segregations within the host rock (Thayer, 1956). For this reason there are no zones of alteration associated with the chromite such as commonly accompany ores that were deposited by solutions passing through older rocks. Thus concealed deposits are difficult to detect. With very few exceptions the deposits that have been found either cropped out at the surface or were accidentally encountered in excavation. Ordinarily the ore bodies have an erratic distribution within the host rock and defy attempts at systematic prospecting. However, in many places separate ore bodies occur in clusters; thus areas that contain known deposits are more favorable for prospecting than apparently barren areas. For a similar reason, shear zones in which chromite deposits have been found are favorable features for prospecting. Shear zones are relatively common features in ultrabasic rocks, representing relief from shearing stresses along zones of weakness, and an ore body or group of ore bodies represents an inherent zone of weak-



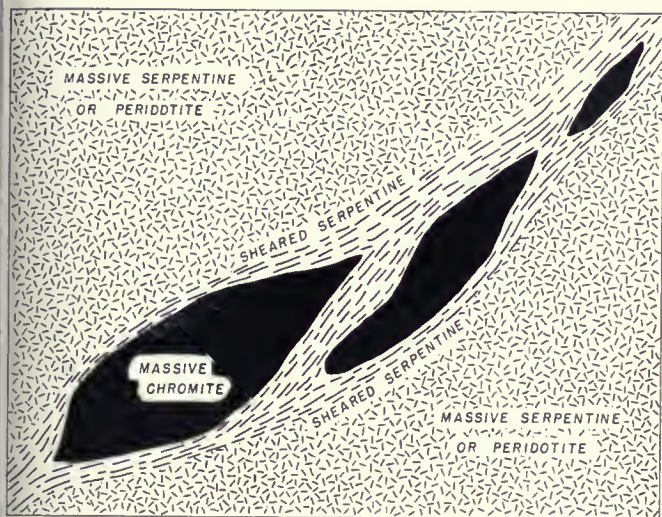


FIGURE 3. Diagrammatic sketch of pods of massive chromite in a shear zone.

ness within the rock mass. In many places in California two or more faulted ore bodies appear to have been part of a single mass of chromite (fig. 3). However, most shear zones in serpentine are developed along other elements of weakness, and do not contain ore.

Many massive chromite ore bodies in California are accompanied or cut by dikes of rodingite, a dense, heavy, greenish white rock. Rodingite is largely composed of vesuvianite and hydrogrossular, and in most places was apparently derived by hydrothermal alteration of pyroxenite dikes. Although it is associated with many chromite deposits, rodingite also occurs in many places in serpentine where no chromite has been found. Thus it has no known genetic relationship with ore deposits.

Because of its high specific gravity and its great resistance to chemical weathering, the chromite that has been released from its parent rock by weathering and erosion commonly accumulates in residual deposits, or becomes concentrated in stream and beach deposits. Such concentrations are locally rich enough to be mined. For the most part, however, the greatest value of chromite float or detritus is that it often can be traced by the prospector to its source. Most of the known deposits have been found in this way.

Geophysical methods have not been used extensively in prospecting for primary chromite deposits and have met with varying success. The discouraging results yielded by the application of magnetic methods have been summarized by Ilawkes (1951), who writes: "Magnetic methods have been applied to chromite prospecting far more often than would seem to be warranted by its generally undistinguished magnetic properties. The writer knows of at least 30 areas where magnetic surveys have been run, but not a single example of commercial discovery of primary chromite that could be credited to the magnetic data." However, the use of gravimetric methods has met with success in Cuba and appears to be quite promising. In the Camaguey district of Cuba, gravimeter surveys led to discovery of a large concealed ore body whose highest point is at a depth of 130 feet (Hammer et al., 1945; Flint et al., 1948).

*Localities in California.* California contains abundant serpentine and peridotite, the host rocks of chromite deposits. As seen in figure 4, these rocks are widely distributed in the Klamath Mountains, Coast Ranges, and foothills of the Sierra Nevada. Chromite deposits have been found in all of the counties in which these rocks crop out (Jenkins, 1942). Altogether, more than 1200 deposits have been found in the state, and approximately 50 of these have each yielded more than 1,000 tons of ore to date. The leading chromite-producing counties, listed in order of total production prior to 1956, are San Luis Obispo, Del Norte, El Dorado, Siskiyou, Glenn, Fresno, and Shasta.

Most of the chromite thus far produced in California has been lump ore from massive deposits. These deposits ranged in size from less than one ton to about 20,000 tons. More than half of the individual ore bodies contained less than 15 tons, and most of the remainder have yielded between 15 and 150 tons. The largest massive ore body found in California, the Little Castle Creek deposit in Shasta County, yielded approximately 15,000 tons of chromite (Matson, 1949).

Most of the deposits that have yielded substantial amounts of massive chromite consisted of two or more closely spaced ore bodies. In places these groups of ore bodies are somewhat aligned in sheared or faulted areas and apparently represent separated fragments from one or more masses that originally were much larger. For example, at the Lambert mine in Butte County, a series of large pods and small lenses and stringers of massive chromite are distributed for at least 215 feet along a prominent and well-defined shear zone in serpentine. The width of the shear zone ranges from less than 10 feet to at least 25 feet. The zone contains at least six known sizable ore bodies, the largest of which was 60 or more feet long and as much as 20 feet wide and contained about 2000 tons of chromite (Rynearson, 1953).

Some ore bodies appear to have been originally emplaced in clusters, with no evidence that shearing has modified their relative positions. An example is the Cyclone Gap deposit in Siskiyou County, where at least seven irregular but elongate pods of massive chromite occur in a cluster, their longer axes oriented approximately vertical. Only one pod, which was well exposed, constituted the original discovery. However, in the process of mining it, five other hitherto unexposed pods were found nearby. The smallest of these ore bodies contained 1 or 2 long tons and the largest approximately 1100 long tons. By 1945 all of these pods had been mined out, yielding a total of 2,429 long tons of massive chromite. The maximum depth of mining was about 120 feet (Wells, et al., 1946). In 1951, an exploratory tunnel was driven into the mountainside to explore the ground below the old workings, and resulted in the discovery of the largest ore body yet found at this deposit. This is a vertical, elongate pod which extends from a thin, vein-like surface exposure, previously undetected, to a depth of at least 180 feet. In cross section it is roughly circular, and about 30 feet in maximum diameter. By 1956, when mined to a depth of about 180 feet, this ore body had yielded approximately 8500 long tons of massive chromite containing 48 to 50 percent  $\text{Cr}_2\text{O}_3$ .

Del Norte County has been the principal source of lump chromite in the state, although all of the chromite-



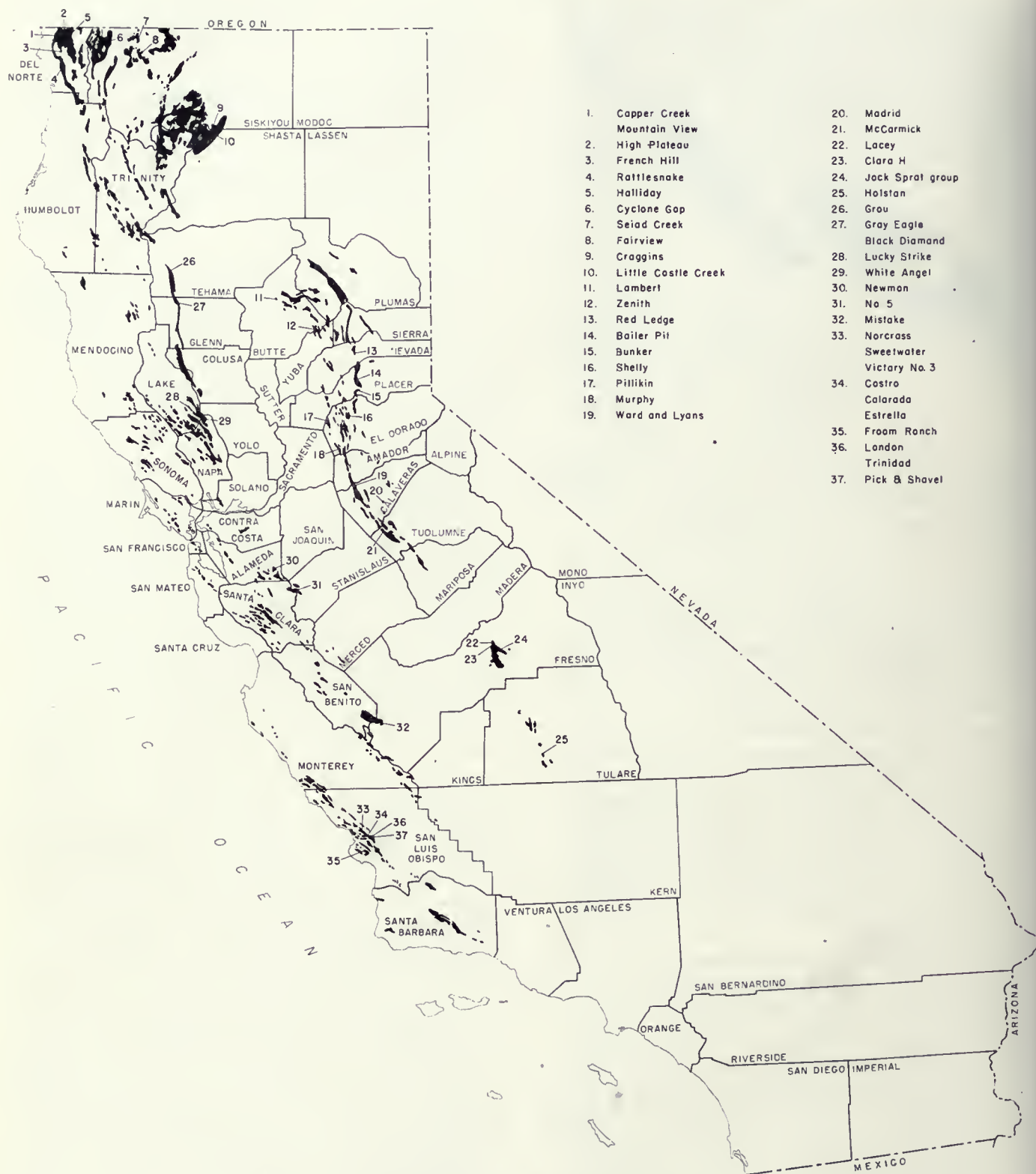


FIGURE 4. Major outcrops of serpentine and peridotite in California, showing locations of the principal chromite mines. All mines indicated have yielded more than 1000 tons of chromite.



producing counties have contributed to our total production of this type of ore. The lump ore has been mostly of metallurgical grade and probably averaged at least 45 percent  $\text{Cr}_2\text{O}_3$ . Many mines have yielded substantial amounts of ore containing 50 percent  $\text{Cr}_2\text{O}_3$  or more.

Most disseminated ore bodies in California are tabular to lenticular masses of serpentinized dunite containing swarms of grains, clots, nodules, or small lenses of chromite. In some deposits the chromite is rather evenly distributed in the host rock; in others the chromite grains occur in streaks or layers. The ore ranges from material consisting principally of chromite to rock containing only a few percent of chromite. Deposits of disseminated ore in California range in size from a few tons to several hundred thousand tons.

Prior to World War II the tonnage of chromite concentrates produced in California was relatively small. However, the high prices caused by war time demand induced the construction of mills at several of the larger disseminated deposits, and since that time concentrates have accounted for an ever increasing proportion of the chromite output of California. Most of these concentrates have come from deposits in San Luis Obispo, El Dorado, and Glenn Counties.

Almost all of the disseminated ore that has been mined contained more than 10 percent  $\text{Cr}_2\text{O}_3$ , and the concentrates generally contained more than 45 percent  $\text{Cr}_2\text{O}_3$ .

With very few exceptions deposits of disseminated chromite ore are mined by open pit methods. Large amounts of waste must be handled in the ore bodies that contain irregularly distributed chromite, that dip gently and have a barren overburden, or that consist of narrow, steeply dipping ore bodies. For example, during World War II the Gray Eagle and adjoining Black Diamond mines in Glenn County yielded 136,440 long tons of ore, from which 30,806 long tons of concentrates were produced. In mining this ore, about 878,000 long tons of overburden was removed, making the ratio of waste to ore about 6.5 to 1 (Dow and Thayer, 1946). In the large open pit operations at the Pillikin mine in El Dorado County, the ratio of waste to ore was commonly about 4 to 1, but in places was more than 8 to 1. Through 1945, this mine had yielded about 17,000 long tons of concentrates in addition to approximately 10,000 tons of lump ore (Cater, et al., 1951).

Known reserves of chromite in California are always relatively small. This is particularly true of massive ore, because such deposits ordinarily are mined simply by following the ore and without drilling or other exploration to establish reserves. Moreover, most massive deposits are small and are mined out quickly. Consequently, most of the known reserves of chromite in California are in disseminated deposits, some of which have been explored by the U.S. Bureau of Mines.

The largest known reserves in the state are in the various ore bodies of the Pillikin mine, El Dorado County, where geological investigations have indicated reserves of approximately 4,500,000 tons of ore containing 10 percent or more of chromite (Wells, et al., 1945). However, this estimate is entirely based on surface examination, without benefit of diamond drilling or other underground exploration.

Trenching and diamond drilling at the Seiad Creek deposit in Siskiyou County indicated reserves of at least

266,000 tons of ore containing 6 percent  $\text{Cr}_2\text{O}_3$  or 60,000 tons containing 15 percent  $\text{Cr}_2\text{O}_3$  (Wiebelt and Ricker, 1949; Wells and Cater, 1950). Recent tests by the U.S. Bureau of Mines indicated that table concentrates containing more than 50 percent  $\text{Cr}_2\text{O}_3$  can be produced from ores of the Seiad Creek mine (Engel, et al., 1956).

An extensive sampling of some of the principal deposits in San Luis Obispo County recently has been described by Smith and Ricker (1951). Other deposits in California for which sampling projects also have been described include the McGuffy Creek deposit in Siskiyou County (Wiebelt, 1949), the Croggins mine in Siskiyou County (Shattuck and Ricker, 1949), the Little Castle Creek deposit in Shasta County (Matson, 1949), and the McCormick mine in Tuolumne County (Shattuck and Ricker, 1949a).

Chromite is one of the strategic minerals for which exploration loans may be obtained from the U.S. Defense Minerals Exploration Administration. After a chromite prospect has been approved for such a loan, this agency will pay 50 percent of the cost of exploration. Up to July, 1956, the only such loan approved to explore for chromite in California was granted to the operators of the Lambert mine in Butte County.

*Utilization.* The utilization of chromite is based both on its chemical and its physical properties. It is the only commercial source of chromium, which is of value both as a metal and as a constituent of many industrial chemicals. In addition, the high melting point and neutral chemical nature of chromite make it of great value as a special refractory material. Thus, the uses of chromite fall into three main groups: metallurgical, refractory, and chemical. A different type of ore is ordinarily best suited to each of these three uses, but high-grade ores may be used interchangeably to a certain extent.

In the metallurgical field chromite is used in the production of ferrochromium, the medium by which chromium is added to ferrous alloys. The two principal types of ferrochromium, low-carbon and high-carbon, are produced by reducing chromite ore in an electric furnace. High-carbon ferrochromium, the cheaper of the two, is suitable for the addition of chromium to low alloy steels in which carbon must commonly be present. Low-carbon ferrochromium is required in the manufacture of higher chromium steels, such as stainless steels, where a high carbon content is detrimental. In at least one process, of somewhat limited application to date, chromite is added directly to the steel furnaces.

When alloyed with iron and certain other metals, chromium imparts certain desirable properties that make it essential to the steel industry and to military preparedness. As an alloying agent, chromium commonly is used alone to profoundly modify the properties of ordinary carbon steel. It also is used with other alloying elements, such as nickel, tungsten, cobalt, vanadium, and molybdenum (Udy, 1956, vol. 2). When alloyed in proper amounts with iron, chromium imparts to the resulting steel a great resistance to oxidation and corrosion. All stainless steels contain chromium in proportions ranging from 11 percent to about 30 percent. For decades following its discovery in 1914 stainless steel was largely limited in use to the manufacture of cutlery. However, in recent years new applications, particularly



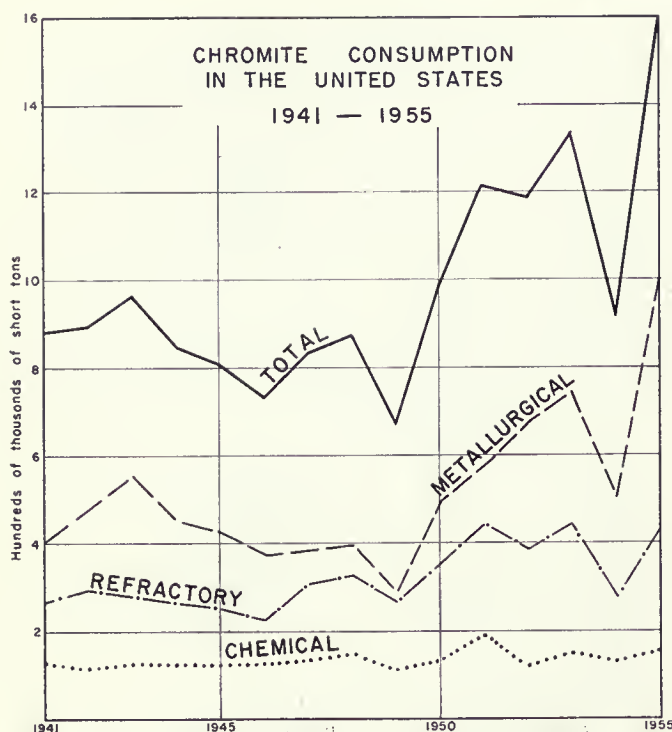


FIGURE 5. Chromite consumption in the United States, 1941-55, indicating amounts used for metallurgical, refractory, and chemical purposes.

in the manufacture of appliances and in the construction industry, have greatly increased the use of stainless steel.

As a constituent of steel, chromium also increases hardness, toughness, susceptibility to magnetism, and strength at high temperatures. Thus chromium steels are invaluable in the manufacture of such articles as armor plate, projectiles, high speed cutting tools, transmission parts, and machinery subject to abrasive action and high temperatures, such as jet engines and gas turbines.

For metallurgical purposes, industry traditionally desires chromite that contains at least 48 percent  $\text{Cr}_2\text{O}_3$  (chromic oxide) and with a ratio of the weight of chromium to iron in the ore of approximately 3 to 1. However, lower grade ores commonly have been used during recent years (Katlin and Heidrich, 1955). The silica content should be low and the combined content of alumina and magnesia is preferably lower than 25 percent. Hard lump ore is usually considered desirable for this purpose, although fines or concentrates may be used for the production of low-carbon ferrochrome. The metallurgical grade chromite that is used in the United States is obtained principally from Turkey and Southern Rhodesia.

Chromite is also used extensively in the manufacture of refractory bricks and plastic cements (Heuer, et al., 1956). It has a high melting point and is chemically almost neutral; consequently it resists attack by both acids and bases at high temperatures. Thus chromite bricks, plastic cement, and ramming mixtures are widely used for lining and repairing metallurgical furnaces, particularly in steelmaking furnaces. For refractory purposes, a high  $\text{Cr}_2\text{O}_3$  content is not necessary if it is

compensated for by alumina. However, the combined  $\text{Cr}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$  content should be 57 percent or more. The silica content should be below 5 percent and the iron content also should be low, preferably below 10 percent. Hard, lumpy ore is desirable so that it can be ground to certain specifications, but fines and concentrates may be used if necessary. Almost all of the refractory grade ore used in the United States in recent years has been imported from the Philippines.

Chromium chemicals are obtained by calcining a mixture of finely ground chromite, limestone, and soda ash. Water leaching of the resulting calcine yields sodium chromate solution from which sodium dichromate is obtained by treatment with carbon dioxide or sulfuric acid. Sodium dichromate, the prime product of the industry, is then converted into chromic acid and other chromium chemicals (Copson, 1956). Perhaps the most obvious application of chromium chemicals is the thin chromium plating on automobile bumpers and other fittings. These protective coatings are applied to the steel fittings by electrodeposition in a chromic acid bath. However, the principal uses of chromium chemicals are for leather tanning and for the production of certain pigments, for which no satisfactory substitutes are known. Chromium chemicals are also used in the manufacture of such materials as pyrotechnics, matches, mordants, photographic supplies, wood preservatives, dry cell batteries, and corrosion-inhibiting muds for oil well drilling (Udy, 1956, vol. 1).

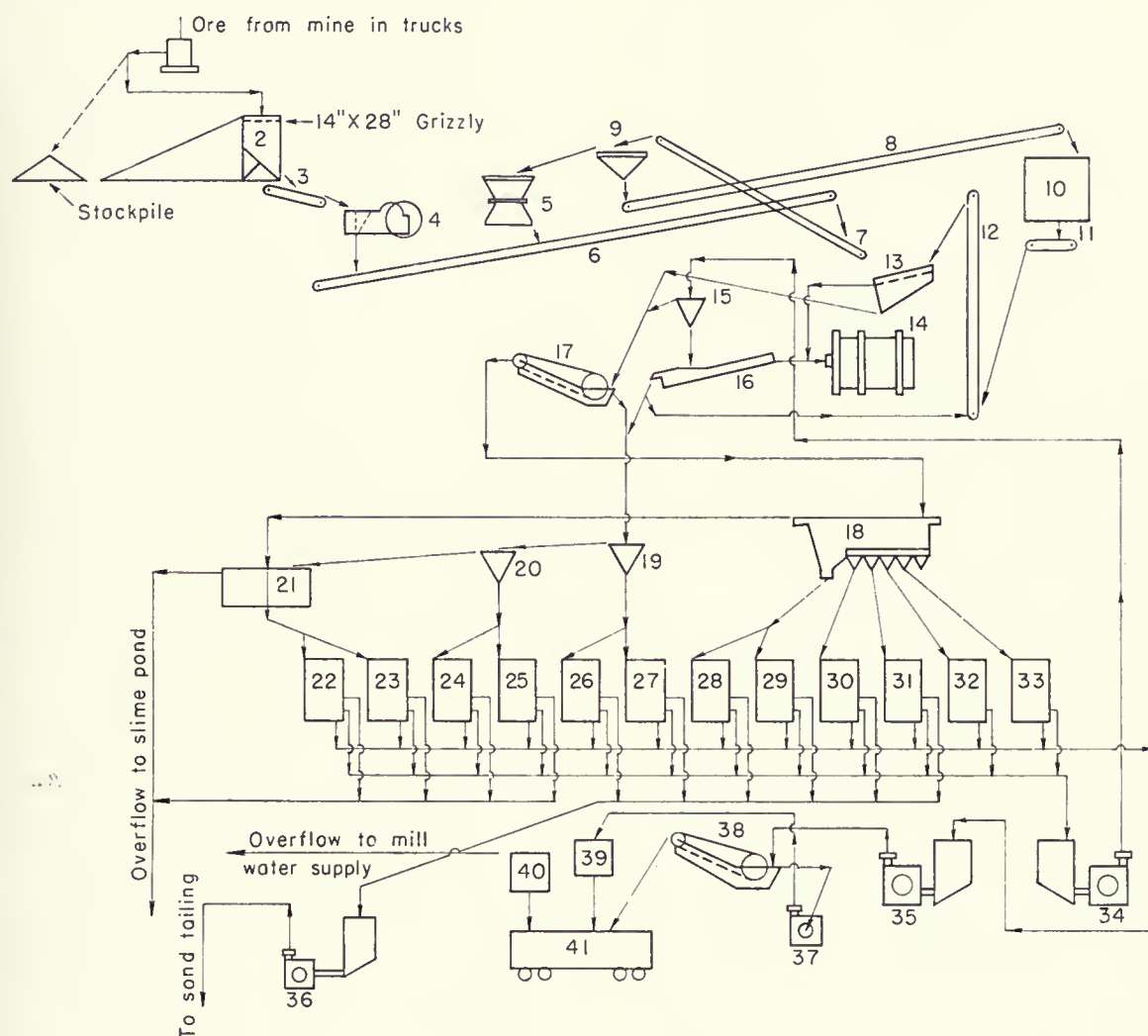
Chemical grade chromite should contain a relatively high percentage of  $\text{Cr}_2\text{O}_3$ , preferably over 44 percent, but the iron content can be much higher than for metallurgical or refractory purposes. Thus the chromium-to-iron ratio of chemical grade ores is commonly as low as 1.5 to 1. The silica content should be less than about 8 percent. Fines or concentrates are used in order to facilitate disintegration during processing of ore for chemical purposes. In recent years all chemical grade chromite used in the United States has been obtained from the Union of South Africa.

During 1955 the amounts of the three grades of chromite consumed in the United States were: metallurgical, 993,653 short tons; refractory, 431,407 short tons; chemical, 158,923 short tons (McInnis and Heidrich, 1956).

*Mining Methods and Treatment.* The methods of mining and treatment of chromite ores are determined by the character of the ore being worked. Most of the chromite produced in California has been massive lump material. This is mined by open cut or underground methods, depending on the position, size, and shape of the ore body. The ore is hand-sorted and shipped without further treatment.

Almost all of the disseminated ore has been mined by open cut methods. The concentration of chromite ores is generally a relatively simple process in that chromite is the principal heavy mineral and the gangue minerals are magnesium silicates which have much lower specific gravities than chromite. The usual method involves primary and secondary crushing, milling, and gravity concentration on tables. Figure 6 is the flowsheet of the relatively large treatment plant at the Castro mine in San Luis Obispo County. Most operations are smaller,





1. Truck scales
2. Crude ore bin
3. 36" Apron feeder
4. Jaw crusher, 15"X30"
5. Gyratory crusher
- 6.-8.incl. 16" Belt conveyor
9. Flat screen, 4'X6' single deck  
1 1/4" X 1 1/2"
10. Wooden tank bin, about 100 tons  
live capacity
11. 16" Belt feeder
12. 14" Belt elevator
13. Screen, 3'X6' single deck, 20 mesh
14. 6'X4' Low discharge ball mill
15. Surge box
16. 21"X16" classifier

17. 16" Belt sand drag
18. Sizer, 6 compartments
19. 5' diameter, 50° cone
20. 6' diameter, 50° cone
21. 14'X10' Thickener, simplex  
diaphragm pump on underflow
- 22.-33.incl. 12 Tables, concentrating
34. 2" Pump
35. 1" Pump
36. 2" Pump
37. 1" Pump
38. Sand drag, 8" belt, 9" L flights
- 39.-40. Two settling boxes,  
each 6'X12'X5' deep
41. Standard gage R.R. cars.

FIGURE 6. Flowsheet, chromite treatment plant, Castro mine. (From Smith and Ricker, 1951.)



consisting of two to four tables which directly receive the ball mill product. Jigs, heavy media separation equipment, and the Humphreys spiral concentrator are also used, although the latter two are not utilized in California. Magnetite is a troublesome mineral in some ores because it settles with the chromite and may lower the value of the concentrate both by dilution and by increasing the iron content.

As some chromite ores contain too much iron to be marketable, even after mechanical concentration, the U. S. Bureau of Mines has experimented with methods to utilize them. One process involves beneficiation of concentrates by roasting and acid leaching of the reduced iron, resulting in upgrading the chromium content (Lloyd, et al., 1946). Another investigation developed a process for the electro-winning of chromium from domestic low-grade ores, and involves the production of chromium sulfate electrolyte. The chromium is recovered by electrodeposition from the electrolyte (Lloyd, et al., 1946; Sully, 1954, pp. 31-36). Neither of these processes is being utilized in California.

**Markets.** All of the chromite currently being produced in California is sold to the United States Government through the Emergency Procurement Service of the General Services Administration. This agency maintains a purchasing depot at Grants Pass, Oregon, and also purchases chromite in carload lots at the railhead nearest the mine. Prices paid are based on \$115 per long ton for lumpy ore and \$110 per long ton for fines and concentrates, all containing 48 percent  $\text{Cr}_2\text{O}_3$  and having 3 to 1 chromium to iron ratio. Premiums of \$4 per ton are paid for each 1 percent of  $\text{Cr}_2\text{O}_3$  content above 48 percent and for each one-tenth increase in chromium to iron ratio above 3 to 1 up to and including 3.5 to 1. Penalties of \$3 per ton are assessed for each 1 percent of  $\text{Cr}_2\text{O}_3$  below 48 percent down to and including 42 percent, and for each one-tenth decrease in chromium to iron ratio below 3 to 1 down to and including 2 to 1. No ore is accepted that contains less than 42 percent  $\text{Cr}_2\text{O}_3$ , more than 10 percent silica, or which has a chromium to iron ratio less than 2 to 1.

This program was initiated in August 1951, with the intention of purchasing 200,000 long tons of domestic chromite ores and concentrates, which were to be stock-piled for use in emergency. It is scheduled to terminate on June 30, 1959, or when 200,000 long tons of chromite have been received and accepted. According to information released by General Services Administration, 108,946 long tons of chromite had been accepted as of December 30, 1955.

During the time this program has been in effect, the maximum open market price paid for foreign ores assaying 48 percent  $\text{Cr}_2\text{O}_3$ , 3 to 1 Cr-Fe ratio, delivered to Atlantic ports, has ranged between \$52 and \$55 per long ton. Lower grade ores, including those utilized for refractories and chemicals, ranged down to \$22 per long ton.

There are no industrial markets for metallurgical or chemical grade chromite in California because ferrochromium producers and chromium chemical plants are located in the eastern part of the United States. Chromite is used in the manufacture of refractory products by the following California companies (Katlin, 1955): General Refractories Co., Los Angeles; Harbison-Walker

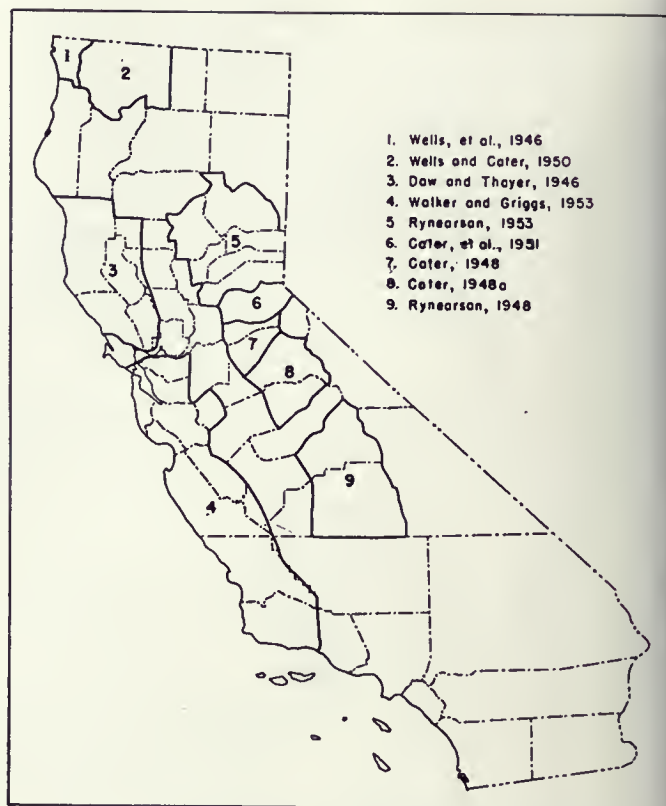


FIGURE 7. Index map showing areas for which descriptions of chromite deposits are published.

Refractories Co., Warm Springs; Kaiser Aluminum & Chemical Corp., Moss Landing; E. J. Lavino & Co., Newark.

Most or all of the chromite used for refractory purposes in California is imported from the Philippines. Late in 1955 a nominal price of \$25 per long dry ton was reported by American Metal Market for refractory ore containing 34 percent  $\text{Cr}_2\text{O}_3$ .

**Production History of Chromite in California.\*** The beginning of chromite production in California, as in Maryland, Virginia, and Pennsylvania, is linked with the Tyson family of Maryland. Isaac Tyson, Jr., in the early eighteen hundreds, studied chromite in the French literature and examined the first known American locality near Baltimore, Maryland. Knowledge of its geological occurrence led him to the exploration of the serpentine belt of the Appalachians, and the location of numerous deposits, some of very large size. Subsequent mining of these properties under lease or purchase gave the family virtual control of chromite production in the United States and it was actually a world monopoly for over 30 years. The ore was shipped to Glasgow, Scotland, to be processed for pigments, dyes, and chemicals, till 1845, when a plant was started near Baltimore by Tyson (Glenn, 1895).

The first chromite ore mined in California was obtained from deposits in Del Norte County which had been discovered by a Tyson Company employee. Beginning in 1869 and continuing for 20 years, ore was shipped

\* Extracted and modified from section on chromite by Richard A. Crippen which appeared in California Div. Mines Bulletin 156, 1950.



round the Horn to Baltimore at the rate of 1,500 to 2,000 tons annually. Deposits in San Luis Obispo, Placer, Mono, and Calaveras Counties also yielded ore in this period.

Importations of Turkish chromite, accompanied by the tariff removal in 1894, brought the domestic price so low that the production of chromite in California ceased from 1896-99, inclusive. Production was small during the years following, most of it being used for refractory lining at California copper smelters; but during the period 1916-18, war-time demand caused 175,277 tons of chromite ore to be shipped from California mines, largely to eastern steel plants. From 1921-41, a yearly average of less than 500 tons of chromite ore was mined in California. Chromite production in the state rose during World War II, and in the period 1941-45 a total of 157,519 tons was obtained. Then followed a severe decline in production, which ended with the resumption of stockpiling of domestic ores by the government in August 1951.

The stimulus created by the incentive prices offered under the present government purchasing program has led to the reopening of many of the chrome mines in California and to the development of several new deposits. California production rose from 404 short tons in 1950 to 30,661 short tons in 1954, but dropped to 22,077 short tons in 1955. San Luis Obispo, Del Norte, and Siskiyou Counties accounted for more than half of this recent production, but most of the chromite-bearing counties contributed to the total. Perhaps the most notable recent development has been the increased exploitation of deposits of disseminated ore to the extent that the tonnage of concentrates produced during 1954 and 1955 considerably exceeded that of lumpy ore.

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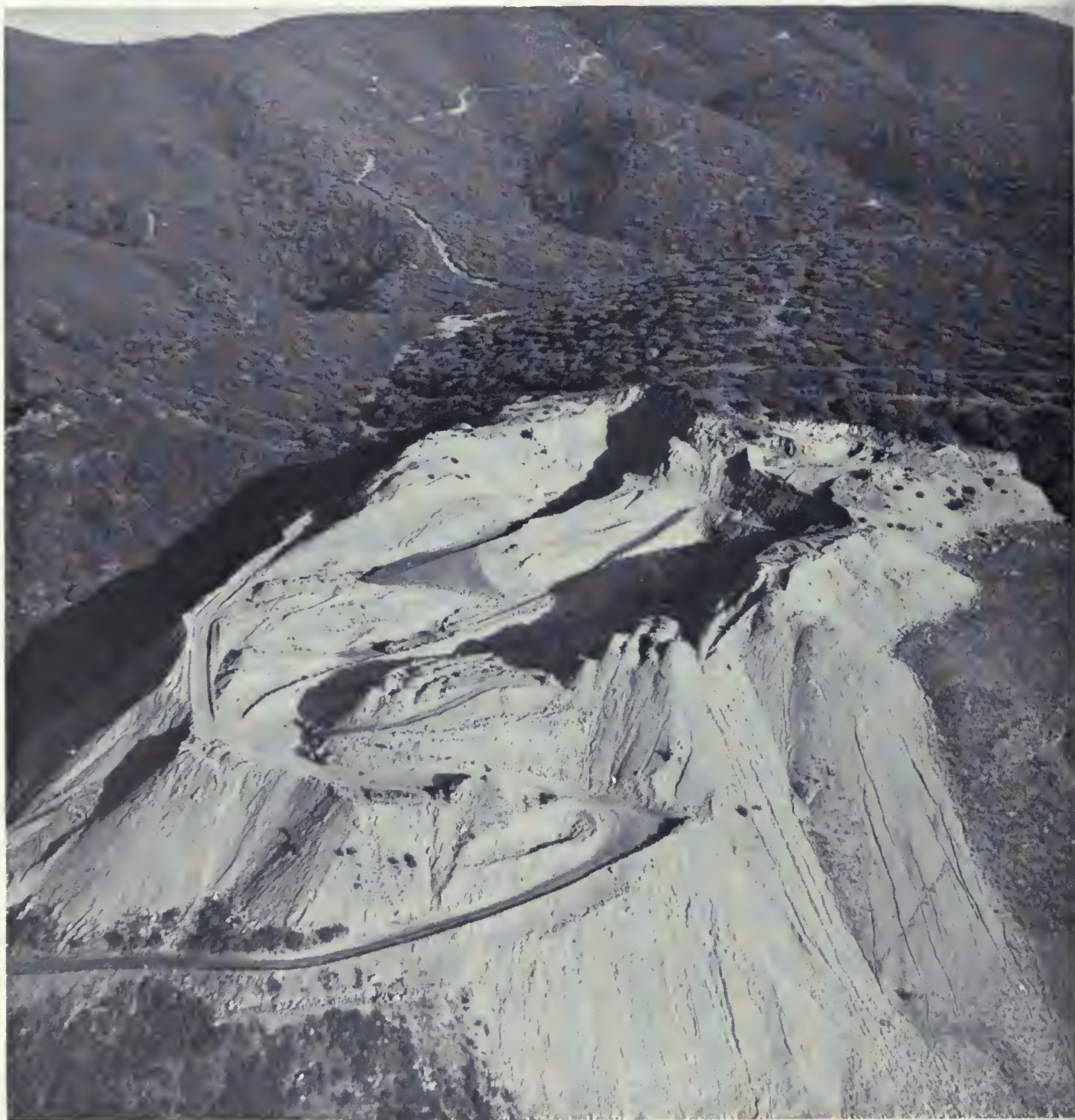


FIGURE 8. Aerial view east toward the Castro chromite mine, San Luis Obispo County. This open pit mine has yielded approximately 120,000 tons of disseminated ore from 4 large ore bodies and several small ones. Largest ore body found contained about 22,000 tons. Average chromic oxide content of the ore before milling was 23 percent. *Photo by McLain Studio, San Luis Obispo, courtesy Durand A. Hall.*



## CLAY

By GEORGE B. CLEVELAND

Clay ranked seventh in volume and tenth in dollar value in California's total mineral production in 1954. During the period 1940-54, clay production in the state increased from 324,399 short tons worth \$687,871 to 2,722,850 short tons worth \$6,038,174. An all-time high of nearly 3 million tons was obtained in 1955. Since 1937, the average value per unit volume of clay produced in California has remained at about \$2 per ton.

California yields annually more than 2 million tons of common clay which is mined from Recent floodplain and alluvial deposits and from Mesozoic shale. Common clay production is centered in the Los Angeles and San Francisco metropolitan areas.

The yearly production in California of fire clays amounts to about 500,000 tons. These clays are of residual and sedimentary origin, and of Eocene and Paleocene ages. They are mined along the western foothills of the Sierra Nevada and around the northern part of the Santa Ana Mountains south of Los Angeles. Sedimentary fire clays also occur in a narrow belt in eastern Alameda County near San Francisco. Fire clay of hydrothermal origin occurs at Hart in eastern San Bernardino County, near Casa Diablo Hot Springs in southern Mono County and in Jawbone Canyon in Kern County. Small amounts of ball clay are mined from the central Sierra Nevada foothill belt. From 10,000 to 15,000 tons of bentonitic clay is produced annually in California and is obtained principally from the Mojave Desert—Owens Valley region and from San Benito County south of San Francisco.

### GEOLOGY

#### Clay Minerals and Clay Materials

The term "clay" is applied both to a group of minerals and to a rock. Most clay minerals are hydrous aluminum silicates. Some of them also contain appreciable proportions of magnesium, iron, potassium, calcium, sodium and other alkali and alkaline-earth elements. They commonly have a platy habit and occur in

grains generally less than 2 microns (2 thousandths of a millimeter) in diameter. Although most rocks can be defined in terms of chemical composition and mineral content, "clay" as a rock name has no precise definition, but alludes to certain earthy, fine-grained materials that generally develop plasticity when mixed with limited amounts of water and which contain appreciable proportions of clay minerals. This definition includes sedimentary rocks such as shale and argillite of marine origin, silt and mud accumulation in Recent lake basins, claystone formed by intense alteration of crystalline rocks, and soil formed by surface weathering.

Grim (1953) uses the expression "clay material" for any fine-grained, natural, earthy argillaceous material, including the rocks mentioned above. The physical and chemical properties of the clay material are determined largely by the nature and relative abundance of the clay minerals they contain. The non-clay minerals quartz, mica, limonite, pyrite, calcite, and gypsum are common in most clay material.

Structurally, the clay minerals consist of layers of aluminum and silicon ions or atoms bonded together by oxygen atoms or combinations of oxygen and hydrogen atoms which are between the two layers. The clay mineral particles are held together by electrostatic charges on the surfaces and edges of the particles. Magnesium and iron replace some of the aluminum atoms in some clay minerals. Replaceable sodium, calcium, and potassium ions occur on the surfaces and edges of the clay mineral particles. These replaceable ions or any ions and molecular layers of water between the clay particles determine to a large extent the plastic properties of a clay mineral.

Clays, on the basis of their mineralogy, are grouped under three types: kaolinites, montmorillonites and illites. The kaolinite group includes the minerals kaolinite, dickite, nacrite, halloysite, anauxite, and allophane; all are hydrous aluminum silicates. Montmorillonite, saponite, nontronite, hectorite and beidellite comprise the montmorillonite group and consist of hydrous silicates of aluminum, magnesium, iron and, in some varieties, lithium. Montmorillonites commonly contain calcium and sodium, as replaceable ions. Illite, as a group name, has been applied to the micaceous varieties of clay which are complex hydrous silicates of potassium, aluminum, iron, and magnesium.

The accurate identification of the clay minerals generally requires highly trained mineralogists and elaborate equipment, but a knowledge of the mineralogy, chemical composition and physical properties of a given clay or clay material may help in predicting its ultimate usefulness. A crude evaluation of the possible commercial value of a clay can be obtained by testing for a few common properties such as the swelling ability when immersed in water, the plasticity, and firing properties. A detailed evaluation however, includes the identification of the clay mineral or minerals by one or more of the following methods: staining techniques, optical testing, differential thermal analysis, x-ray diffraction, electron microscopy and infrared spectroscopy.

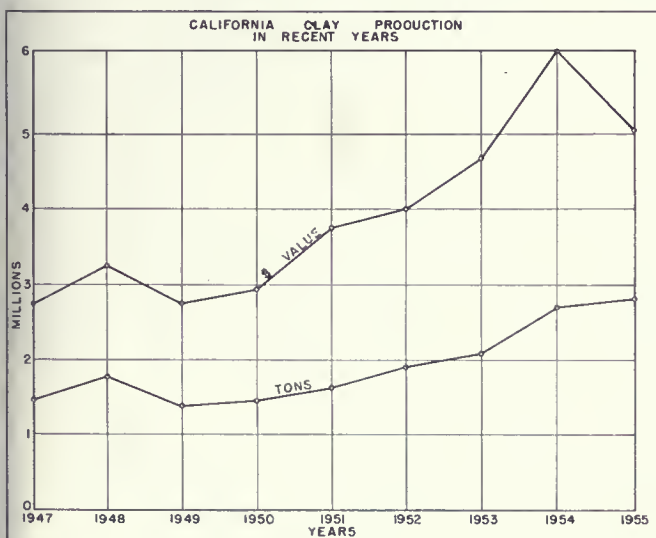


FIGURE 1.



Table 1. *Geologic classification of California clay deposits.\**

Type of deposit by origin	Clay minerals	Texture and non-clay composition	Ceramic properties	Uses	Characteristics of deposits	Extent and distribution in California
<b>I. RESIDUAL</b>						
<b>A. Hydrothermally altered volcanic rocks.</b>						
1. Basic and intermediate volcanic rocks.	Mostly montmorillonite	Massive, compact, commonly small amount of non-clay mineral material which consists of unaltered parent rock.	Plastic; may swell when wet	Bentonite—drilling mud and bonding clay. Adsorbent clay-decolorizer and catalyst.	Deposits commonly a few square miles in area and a few tens of feet thick.	Limited number of known deposits occur mainly in the southern half of the state.
2. Silicic volcanic rocks.	Kaolin group	Massive, compact; commonly small amount of non-clay mineral material which consists of unaltered parent rock.	Refractory; low plasticity	Miscellaneous fire clay and china clay	Deposits commonly a few square miles in area and a few tens of feet thick.	Limited number of known deposits occur mainly in the southern half of the state.
<b>B. Weathered crystalline rocks (volcanic, plutonic, and metamorphic).</b>	Clay mineral composition depends upon composition of parent rock and degree of weathering; intense weathering and leaching yields kaolinite minerals.	Massive, compact, residual structure and texture common except where weathering extreme. Non-clay mineral material consists of unaltered parent rock; quartz grains common where parent rock is granitic or metamorphic; iron oxide content usually high where parent rock is of basic or intermediate composition.	Commonly plastic and somewhat refractory.	Red- and buff-burning variety used in face bricks, sewer pipe, and other heavy clay products; white or pale cream-burning variety used in refractory products.	Deposits cover area of a few square miles and are many tens of feet thick; restricted to zones of intense weathering.	Commercial deposits in Alameda area, Riverside County, and Lone area, Amador County.
<b>C. Soil derived from weathering of all types of rocks.</b>	Kaolin, montmorillonite and illite groups; montmorillonite commonly predominant; illite abundant in soils derived from marine shale.	Friable and granular; commonly contains higher proportion of non-clay material than clay minerals; non-clay mineral portion depends upon parent rocks, but generally includes quartz, iron oxides, and mica.	Commonly plastic, fires red, and vitrifies at a low temperature.	Mostly common brick	Thin veneers covering many square miles.	Widespread throughout the state, especially in areas of high rainfall.
<b>II. SEDIMENTARY</b>						
<b>A. Marine claystone derived from nearby residual clay.</b>	Kaoline group	Commonly massive, compact, some laminated non-clay mineral material consists mostly of coarse, angular quartz grains and carbonaceous matter.	Low to moderate plasticity, carbonaceous varieties commonly highly plastic; refractory; fires white to red depending upon iron oxide content.	White- to pale buff-burning variety used in refractory clay products; red-burning variety used in face brick and sewer pipe.	Deposits underlie areas of a few square miles and are tens of feet thick; sand and iron oxide content variable within deposit.	Occur in Pliocene and Eocene deposits in narrow belts flanking the Santa Ana Mountains in Riverside and Orange Counties and in the Sierra Nevada foothills in Alameda and Placer Counties.
<b>B. Marine shale and claystone derived from large and distant source areas.</b>	All three groups; illite predominant, kaolinite sparse.	Compact, laminated; commonly has high non-clay mineral content, mostly quartz and mica in silt and sand-size particles, small to appreciable amounts of iron oxide, calcite, feldspar and carbonaceous matter.	Commonly moderately plastic, fires red; vitrifies at low temperature.	Heavy clay products including sewer pipe, and common and face brick.	Individual deposits commonly many square miles in area and many tens of feet thick.	Numerous large deposits ranging in age from Jurassic to Pliocene occur mostly in Coast Ranges, Transverse Ranges, and Peninsular Ranges.
<b>C. Lacustrine and alluvial silt and clay.</b>	All three groups present	Friable, laminated, high iron clay mineral content; small to appreciable amounts of calcite and iron oxide.	Moderately plastic; commonly burns red and vitrifies at a low temperature.	Drilling mud, heavy clay products.	Moderately large deposits underlie areas of many square miles and are tens of feet thick.	Dry lakes occur in the desert basins; recent alluvium deposits occur in large and small valleys throughout the state.

\* Prepared by B. H. Rogers, 1956.



Like other materials that have been used throughout much of human history, clay materials have acquired many commercial names. The name generally refers to principal uses, e.g. brick clay or paper clay. A type of clay, however, commonly is named for the locality where it is found, or for a person, or for some specific property that it may possess. Industrial producers have unavoidably complicated the terminology by introducing innumerable trade names. Commercial classifications based on ceramic properties, mineralogy, geologic occurrence, origin, or industrial use have been suggested (Grim, 1953; Ries, 1949; Schrader and others, 1917). Because of the broad interpretation of the term "clay" many of these classifications must be used in a restricted sense.

In spite of the confusing and overlapping terminology, industrial clays can be divided into six main groups based on the simplified classification used by the U. S. Bureau of Mines: (1) kaolin (china clay), (2) ball clay, (3) fire clay, (4) miscellaneous clay (common clay), (5) bentonite, and (6) fullers earth. The first four can be conveniently placed under the heading of "ceramic clay" and the last two under the heading of "bentonitic clay." Ceramic clays are used principally in ceramics, but have many non-ceramic uses as well. Although non-swelling bentonitic clays could properly be termed bleaching or adsorbent clays because of their wide application for this purpose, they also have many other uses. The six groups will be discussed more fully under the heading "utilization and characteristics of industrial clays."

#### Occurrence and Origin

Clay minerals are secondary in origin and develop by the weathering or hydrothermal alteration of parent rocks that generally are rich in alumina and silica. Most clay has formed by the weathering of crystalline rocks that contain abundant feldspar and little iron, such as granite or granitic gneiss.

All igneous and metamorphic rocks are chemically unstable under atmospheric temperatures and pressures because these conditions are quite different from those that attended their formation. Being out of chemical equilibrium they change to more stable forms in response to their new environment. Clay minerals are the stable weathering products of many rock-forming minerals, especially feldspars.

Under the moist and warm conditions of tropical weathering, decomposition of the parent rock is more rapid and complete than in other types of climate. The weathering effects reach deep below the surface and the chemical leaching removes virtually all of the non-clay forming remnants of the original rock. Thus large deposits of nearly pure clay are formed in a relatively short span of geologic time. In areas of temperate climate, large residual deposits of high-quality clay ordinarily do not form, as the alteration and leaching proceeded much more slowly.

Clay deposits are commonly classified by mode of formation as (1) residual deposits which occur at the site of formation, and as (2) sedimentary deposits which contain clays that have been transported, usually by water, and deposited some distance from their site of formation. The residual deposits that are products of weathering form mantles on the parent rock from which they are derived. They ordinarily cover many acres and

range from a few feet to several tens of feet in thickness. The intensity of weathering and the size and shape of the area of exposed parent rock have, in general, determined the size of the clay deposit, whereas the character of the clay is largely determined by the nature of the parent rock. Feldspar-rich pegmatite dikes are altered to clay more easily and to greater depths than are many other rock types. Such clay deposits are generally lenticular in shape and much smaller in total volume than other types.

Clay deposits also can be formed from sedimentary limestones. Clay admixed with limy sediments at the time of deposition may be released by subsequent weathering, forming nearly pure clay deposits. These deposits are generally small and only of local importance.

In general, chemical weathering frees the original elements or compounds in the parent rock (alumina and silica with subordinate sodium, calcium, potassium, magnesium and iron) and they become reconstituted into new minerals—mostly clays. The formation of kaolinite requires the removal of sodium, calcium, potassium, magnesium and ferrous iron (Keller, 1955, p. 48).

Although magnesium, calcium and ferrous iron inhibit kaolinization, they are essential to the formation of the montmorillonite-group minerals. Where these elements are abundant in aluminosilicate rocks and the leaching process is incomplete, montmorillonite tends to form in place of kaolinite. Montmorillonite, unlike kaolinite, generally forms under alkaline conditions. The formation of illite-group minerals requires much the same chemical reactants as do the montmorillonites, but dissolved potassium must also be present in such concentrations as to promote cation exchange.

The hydrothermal alteration of aluminosilicate rocks to clay is accomplished by warm, chemically charged water emanating at depth and derived largely to wholly from igneous sources. This water is conducted through openings to points at or near the surface. En route it leaches the host rocks of soluble compounds and may in turn introduce new materials into the enclosing rocks. In this manner, clay and other mineral deposits are formed. These solutions are thought to be originally acid and to become alkaline upon reacting with the wall rocks. The waters carry chiefly sulfur, carbon dioxide, chlorine and silica. Nearly all of the clay mineral species have been found in hydrothermal deposits.

In hydrothermal deposits, kaolinite commonly is formed by the action of sulfuric acid on aluminosilicate rocks. Hydrogen sulfide gas derived from thermal solutions is oxidized at or near the surface to sulfuric acid. Weak sulfuric acid solutions can form kaolinite, alunite, and free opaline silica, but where there is a meager supply of water, the sulfuric acid becomes concentrated in syrupy films and vigorously attacks the wall rocks. Under these conditions, kaolinite, being an intermediate product in the complete alteration by solfataric action, is chemically unstable and the final alteration products are aluminum sulfate and free silica.

Hydrothermal deposits are generally no more than a few tens of feet in lateral dimensions but commonly extend to much greater depths.

Bentonite, a rock composed principally of montmorillonite-group minerals, appears to have formed largely



Table 2. *Physical properties of selected Ionic clays.*<sup>1</sup>

COMMERCIAL CLAY TYPE	UNFIRED PROPERTIES					FIRED PROPERTIES*												Remarks		
	Color	Water of plasticity (percent)	Plasticity	Dry modulus of rupture (PSI)	Dry shrinkage (percent)	P. C. E.	Cone													
							01			3			8			13				
							Shrinkage (percent)	Total shrinkage (percent)	Adsorption (percent)	Color	Shrinkage (percent)	Total shrinkage (percent)	Adsorption (percent)	Color	Shrinkage (percent)	Total shrinkage (percent)	Adsorption (percent)	Color		
Chaney Hill.....	Blue-gray	31.1	Low	50	3.5	33	7.0	10.5	17.0	Cream	9.0	12.5	9.6	Buff	9.7	13.2	9.7	Buff		At cones 01, 3, and 8 bars showed cracking and were soft and friable.
Ione Red.....	Red and buff	33.8	Good	218	5.6	20-23	7.1	12.7	13.3	Light red	7.6	13.2	12.9	Red	6.9	12.5	11.5	Red		At cones 01, 3, and 8 bars showed no cracking or warping.
Bacon no. 3-4.....	Light buff traces brown	37.1	Very good	252	4.9	32½-33	7.9	12.8	12.8	Light buff	9.8	14.7	4.0	Yellow buff	11.3	16.2	3.5	Yellow buff	Tan	At cones 01 bars showed no cracking or warping; at cones 3, 8 and 13 bars showed no cracking but slight warping.
Bacon no. 5-6.....	Very light buff	32.0	Good	371	5.2	32-32½	8.3	13.5	11.0	Yellow buff	9.5	14.7	7.0	Yellow buff	9.3	14.5	3.5	Yellow buff	Dark tan	At cones 01, 3 and 8 bars showed no cracking or warping; at cone 13 sample showed slight warping.
Irish Hill.....	White	32.4	Poor	68	1.0	32-32½	5.5	6.5	15.2	Light gray	7.5	8.5	10.1	Gray	9.5	10.5	3.6	Gray	White	At cones 01 and 3 bars showed no cracking or warping; at cones 8 and 13 bars showed no cracking but slight warping.

<sup>1</sup> Tests made by the Ceramic Laboratories, University of California, Berkeley, California.

\* Test bars were made from a stiff mud mix and extruded from a laboratory size vacuumed auger machine.



Table 3. Chemical analyses of selected California ceramic clays.

Sample 1, Ross and Kerr (1930, p. 163) ; Sample 2-4,  
Dietrich (1928, p. 354).

	(1)	(2)	(3)	(4)
SiO <sub>2</sub> -----	44.70	45.08	58.36	48.93
Al <sub>2</sub> O <sub>3</sub> -----	38.64	37.31	28.92	36.13
Fe <sub>2</sub> O <sub>3</sub> -----	.96	3.74	2.06	1.15
MnO-----	none	--	--	--
MgO-----	.08	trace	0.12	0.21
CaO-----	.24	0.10	0.66	0.36
K <sub>2</sub> O-----	.14	0.44	0.48	0.87*
Na <sub>2</sub> O-----	.62	0.72	0.45	
TiO <sub>2</sub> -----	.22	--	--	
H <sub>2</sub> O-----	.64	--	--	--
H <sub>2</sub> O+-----	13.88	--	--	--

(1) Kaolinite, Ione, Amador County.

(2) Kaolinite, Alberhill, Riverside County.

(3) Kaolinite, Lincoln, Placer County.

(4) Kaolinite, Tesla, Alameda County.

\* Total alkalies by difference.

by the alteration of layers of volcanic ash, a nearly homogeneous material composed of shards of volcanic glass. The alteration to bentonite probably is effected by ground water, charged with carbon dioxide, organic acids and/or sulfuric acid. The alteration is facilitated by the unstable character of natural glasses. Bentonite also can form fine-grained elastic sedimentary rocks. Many bentonites exhibit, on their weathered surface, a crinkled coral-like appearance. This is commonly called "clay-bloom." It may also extend up through overlying sediments for many feet and crack the soil giving it a particular crosshatched pattern. This texture is best developed in arid regions and is apparently caused by the adsorption of water after partial or complete dehydration (Sebroter and Campbell, 1940, p. 11).

Sedimentary deposits may contain clay derived from any type of residual deposit, and they show a wide range in purity and size. Most sedimentary clay deposits have been transported by water. Streams or currents carry the fine clay and other sedimentary material in suspension and solution, whereas the heavier material ordinarily moves by traction or saltation. During transportation the larger material is reduced in size by abrasion with other particles and with the sides and bottom of the channel. As the material approaches the basin of deposition, whether it be lagoon, flood plain, lake, estuary, delta or

the deep sea, the velocity of the stream or current is gradually checked and its carrying capacity reduced at a somewhat uniform rate. This allows for sorting by particle size with the coarsest fraction deposited first and the clay particles last. However, the volume of water carried by a stream varies, and therefore particles of a given size can be widely distributed. This leads to mixing of particle sizes within the basin and partly accounts for the wide purity range of sedimentary clays. The size and configuration of this type of clay deposit is dependent upon the nature of the basin of deposition. Most sedimentary deposits are narrow lenses that wedge out along the periphery of the basin.

In areas of little relief residual deposits persist and the eroded clay is commonly deposited in nearby basins. As the carrying capacity of the streams is at a minimum, they will selectively remove, transport and deposit the clay rather than the coarser and heavier materials, thereby resulting in nearly pure clay deposits. Bogs commonly form in low areas, and clay and dead plant material are deposited contemporaneously. For this reason coal seams occur in many clay deposits. The presence of organic material causes any insoluble ferric iron in the clay to be reduced to the soluble ferrous state (Bateman, 1942, p. 236). However, sulfide ions also combine with the iron and form insoluble iron sulfides (commonly pyrite) which are deposited with the clay (Keller, 1955, p. 49).

#### Fire-Clay Deposits Associated with Paleocene and Eocene Formations

During the Paleocene and Eocene epochs, California's climate was warm and moist and much of the present land surface was inundated by shallow seas. These conditions favored deep chemical weathering and the deposition of sedimentary clays in the lagoons that bordered the inland seas. During this time the principal deposits of high-grade ceramic clays in California were formed. The clay-bearing Ione formation is exposed along the eastern margin of the Great Valley of California, and the Tesla formation is correspondingly exposed on the western margin. These two sedimentary units are similar and may be separate occurrences of the same formation. The most productive of their contained sedimentary clay deposits are at Ione in Amador County, Lincoln in Placer County, and at Tesla in Alameda County. In Riverside and Orange Counties, residual and sedimentary clay deposits, both of probable Paleocene age, crop out in an arcuate area around the northern part of the Santa Ana Mountains. The most productive of these deposits is at the southeast end of the Temescal Valley near the town of Alberhill. The sedimentary deposits are part of the Silverado formation.

**Ione-Lincoln Area.** The middle Eocene Ione formation crops out in a discontinuous belt bordering the western foothills of the Sierra Nevada, from approximately the Feather River in the north to the San Joaquin River in the south. The Ione formation consists mostly of sand and clay-sand mixtures, with local beds of clay, shale, siliceous gravel, conglomerate and lignite. The formation was deposited in a lagoon environment and therefore shows a wide range in thickness and lithology within a given basin and from one basin to another. The clay-rich bodies occur as beds and lenses and com-

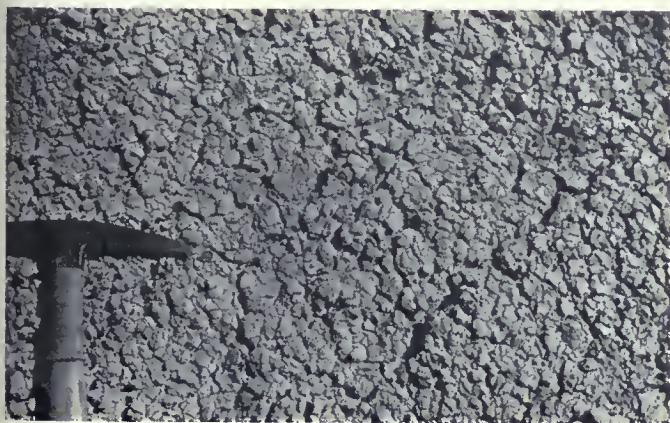


FIGURE 2. Surface of bentonite outcrop showing coral-like texture called "clay bloom." Vallecitos bentonite deposit, San Benito County.



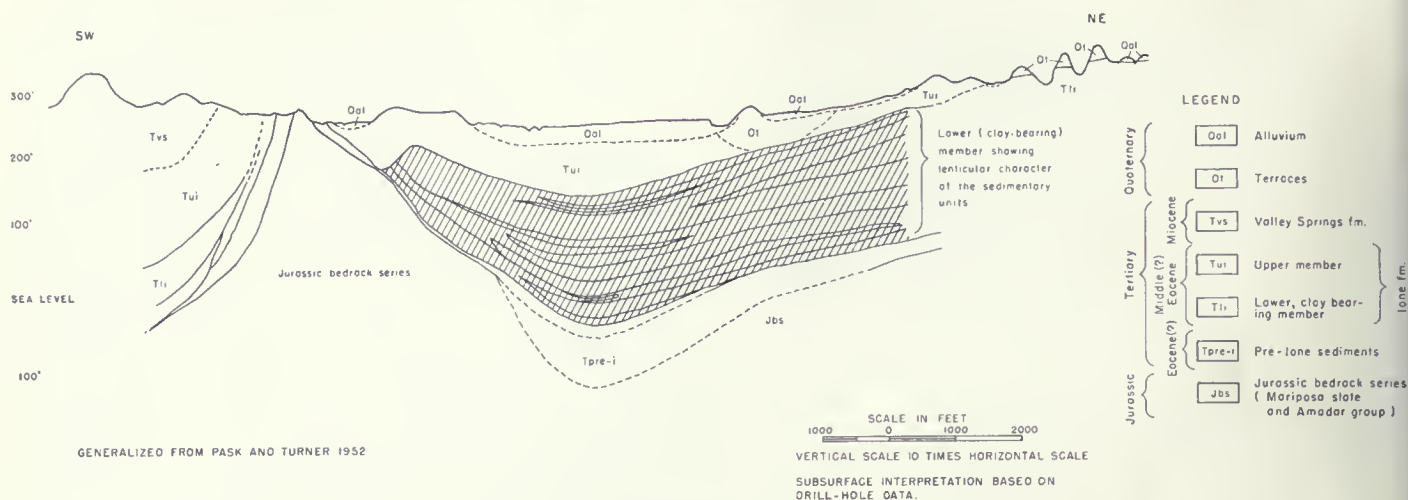


FIGURE 3. Generalized cross section through the Ione area near Buena Vista, Amador County.

monly consist of clay-sand mixtures with a sand content that ranges from a few percent to 60 percent. Other beds within the Ione formation are composed essentially of sand and a small proportion of anauxite (Allen, 1929). Although most of the clay is of sedimentary origin, and was derived from the crystalline rocks of the Sierra Nevada, minor residual deposits are developed on Jurassic metamorphic rocks adjacent to the Ione deposits.

The Ione formation in the Ione area consists of two members, and has a total thickness of about 400 feet. The lower member consists principally of clayey sand, clay and lignite. The upper member is characterized by sand, clayey sand, some clay and minor amounts of conglomerate. Most of the commercial clays are in the lower member and they are either kaolinite or anauxite, mixed with iron oxide and quartz impurities. To the west, the Ione formation is buried by younger sedimentary rocks. Along the foothills to the east in many places the formation is capped by younger volcanic rocks.

Near Ione are 33 clay pits distributed in an area about 12 miles long and 2 miles wide. This area has yielded about one-third of the fire clay produced in California since mining began about 1860. The Ione sediments in this area appear to have filled an irregular basin in Upper Jurassic metamorphic rocks of the Amador group and Mariposa formation. This embayment of the Eocene sea inundated the Ione area and received the clay-rich sediments transported by streams from higher ground to the east. The purer and more refractory clays were deposited on the western side of the basin. Near Buena Vista the Ione overlies unnamed pre-Ione sedimentary rocks. The Ione formation crops out irregularly and is overlain largely by pyroclastic rocks of the Miocene Valley Springs formation and by Recent alluvium. The Ione formation and the post-Ione rocks are nearly free from structural complexities, but have a regional western dip of about 4 degrees.

The clays produced in the Ione area are fire clays and they have been classified into six types based on their ceramic properties. They are the Edwin, Cheney Hill, Bacon, Yosemite, Ione sand (from 25 to 80 percent clay) and Ione Red. As these clays were deposited in local depressions on the bedrock or on the underlying Ione sedimentary rocks the bodies are discontinuous. The clay

bodies range in thickness from a few feet to 30 feet or more but average about 15 feet.

In recent years Gladding, McBean and Company, Pacific Clay Products Company, Western Refractories Company and the Calaveras Cement Company have been actively mining clay in the Ione area. Most of the fire clay is mined for use in heavy clay products; however, a significant tonnage of Edwin-type clay is used in refractory products. Open pit methods are used to mine the clay. In the past, certain of the highly refractory clays were selectively mined underground, when contamination was a factor or when it was not economically feasible to strip off the overburden. The amount of overburden that must be removed to reach the clay varies from a few feet to 25 feet, rarely as much as 50 feet or more.

In the Lincoln area of western Placer County, about 40 miles northwest of Ione, fire clay also is mined from the Ione formation, which here is overlain by the Miocene Mehrten formation. The clay zone, which is about 100 feet thick, is nearly horizontal and is distributed over an area of about four square miles. The Lincoln clays are uniform in thickness and quality over a large portion of the area. The overburden ranges from ten to twenty feet thick and consists of andesite-agglomerate and impure sand and clay. The principal mining activity in the Lincoln area has centered about three large pits developed by Gladding, McBean and Company and Lincoln Clay Products Company, Incorporated. Production of clay began in this area about 1875.

In recent years clays of the Ione formation also have been mined at Valley Springs, Calaveras County; Knights Ferry, Stanislaus County; Michigan Bar and Folsom, Sacramento County; and near Cooperstown, Tuolumne County.

*Alberhill and Northern Santa Ana Mountain<sup>1</sup> Areas.* The Alberhill area, in the northeastern part of the Elsinore quadrangle and at the southeast end of the Temescal Valley, Riverside County, contains the largest known deposits of commercial fire clay in southern California. These deposits have been developed by twenty-four clay pits south of the town of Alberhill and are lo-

<sup>1</sup> Discussion of Alberhill deposits prepared by B. H. Rogers, 1956.



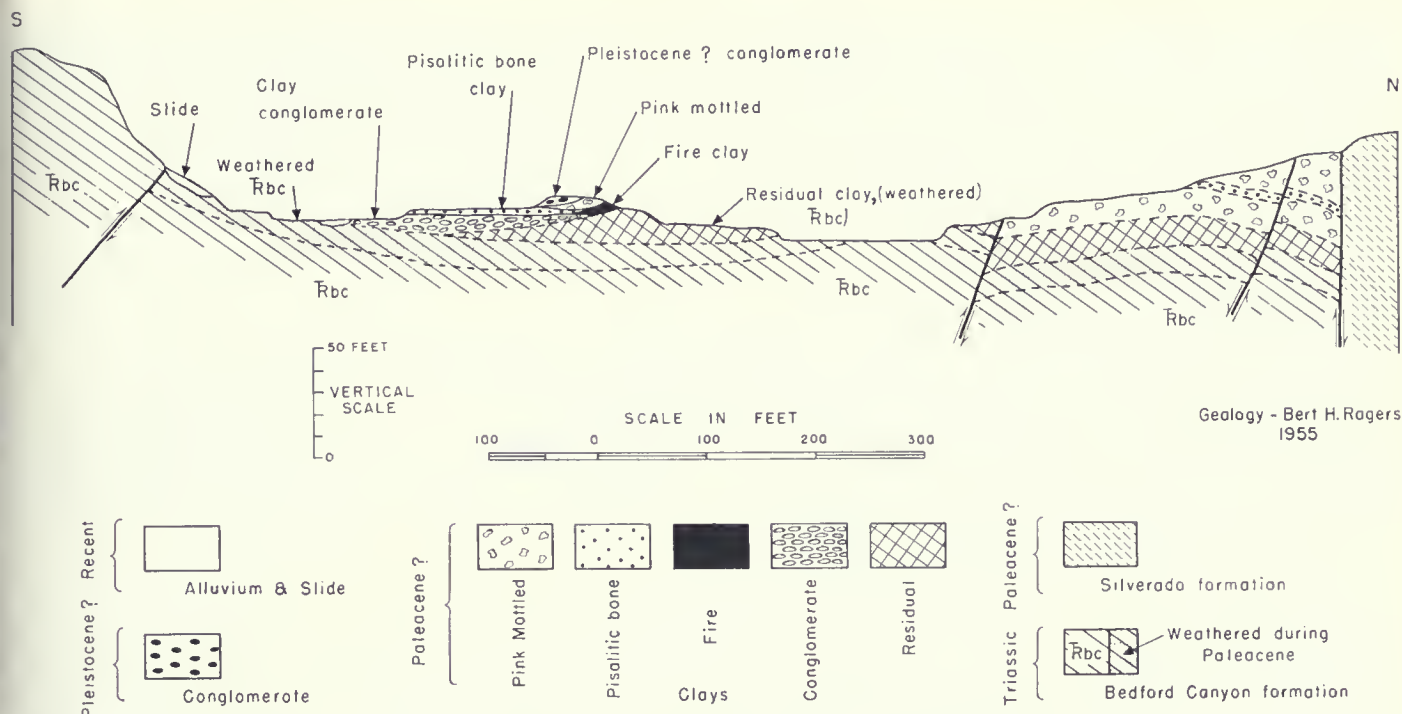


FIGURE 4. Geologic cross section through typical clay pit near Alberhill, Riverside County.

eated in secs. 21, 22, 23, and 26, T. 5 S., R. 5 W., S. B. M. In 1955, twelve pits were active and were operated by the Alberhill Coal and Clay Company, Los Angeles Brick and Clay Products Company, and Gladding, McBean and Company.

The clay deposits in the Alberhill area are confined to a single zone which contains both residual and sedimentary clay. The residual clay was formed by the deep weathering of the Mesozoic crystalline bedrock, apparently in Paleocene time. The sedimentary clay was eroded and transported from the ancient surface and is now part of the Silverado formation of probable Paleocene age. In the Alberhill area this clay-bearing zone underlies an area of about  $1\frac{1}{2}$  square miles along the borders of and within the Temescal Valley. It is about 80 feet in average thickness and has a maximum thickness of about 150 feet. The known deposits of high-grade commercial clay are confined to the areas of the clay pits which total less than half of the area known to be underlain by the clay-bearing zone.

The residual clay deposits are as much as 130 feet thick, and grade downward and laterally into weathered metasedimentary rocks of the Triassic Bedford Canyon formation and andesitic rocks of the Jurassic (?) Santiago Peak volcanics. Slaty cleavage, outlines of feldspar phenocrysts and of angular rock fragments, and hexagonal quartz grains are remnant structures that indicate that the residual clay was derived from slate, volcanic breccia, and hypabyssal igneous rocks respectively.

Although sedimentary clay occurs throughout the 120 feet maximum exposed thickness of the overlying Silverado formation, the layers of clays of commercial importance generally occur in the lower half. Individual layers are commonly less than 20 feet thick and comprise areas of less than 30 acres. Layers of sandy, non-

commercial material occur interbedded with the clay throughout the section.

In most of the area, the Silverado formation is overlain by Quaternary conglomerate that is about 10 feet in average thickness and locally as much as 50 feet thick. In open pit operations this waste material must be removed to expose the commercial clay.

The clays of the Alberhill area are used in two main types of clay products. Red-burning residual claystone, the red and white mottled sedimentary claystone and waxy clay shale are used to make heavy clay products such as sewer pipe, face brick, and tile. White "bone" clay and sedimentary fire clay are used in the production of refractory clay products such as fire brick, flue lining, and, in lesser amounts, pottery.

Clay was discovered in the Alberhill area in the early 1880's. In the early days it was mined by underground methods in which hand tools and man and mule power were employed. Since about 1940, clay has been mined almost entirely by open pit methods. Although modern equipment such as bulldozers, and power shovels are now used to mine almost all of the clay used in heavy clay products, the higher-grade fire clay is still selectively mined by hand methods so that it can be kept separate from the sandy clay.

More than 800,000 tons of high grade clays have been mined in Orange County since 1925. A considerable part of this output came from the Claymont area which is seven miles west of Corona and in the northernmost part of the Santa Ana Mountains. Flint fire clay is mined from beds of the Paleocene (?) Silverado formation. The clay zone strikes nearly north and dips 25 degrees west, and is characterized by ferruginous pisolitic clay. In some places the ferruginous clay is overlain or grades laterally into light-colored flint clays. Pisolitic flint clay





FIGURE 5. Fresh exposure of clay and lignite in upper pit at Alberhill clay mine, Riverside County. Photo by Richard H. Jahns.

is called "bone clay." In some places the clay zone is overlain by lignite and in some localities a high-grade, soft, white to gray clay occurs between the flint clays and the lignite. The contacts between the clays are gradational and the quality of the clay may vary rapidly along the strike. The commercial fire clay is from 4 feet to 7 feet thick, and is hard, gray to black in color and has a conchoidal fracture. It contains disseminated quartz grains, lenses of quartz sand and chlorite. The commercial clay of the Claymont bed is highly refractory, and has been reported to be cone 33 or 34 (Dietrich, 1928, p. 141; Sutherland, 1935, p. 81). Most of the cone 33 to 34 clay has been mined out, but large reserves of lower grade clay remain. The mines were being operated in 1955 by two main tunnels with appended drifts into clay beds overlying the Claymont bed. The clay was recovered by stoping. The Claymont mines have been in nearly continuous operation since Gladding, McBean and Company acquired the property about 1925.

In southern Orange county, southeast of El Toro, small amounts of high grade kaolin are produced from the Schoeppe and from the Arnold properties. This clay is recovered by the hydraulic treatment of a clay-sand mixture from the Silverado formation.

**Tesla Area.** The middle Eocene Tesla formation is confined to a narrow belt. 5 miles long and about one-half mile wide, in Corral Hollow, eastern Alameda and western San Joaquin Counties. The formation is composed of white and buff sands, lignite, carbonaceous shale, and

white to bluish anauxitic clay. The Tesla formation rests unconformably on the Upper Cretaceous Moreno Grande formation and is unconformably overlain by the upper Miocene Cierbo formation and Recent alluvium. The rocks of the Tesla formation and associated formations are folded into a tight east-trending syncline. The south flank is exposed along Corral Hollow where it dips steeply—a factor that has limited the economic development of the clay deposits. The north flank is not exposed. The clay is associated with white sands that lie above lignitic coal beds in the upper part of the formation. The clay ranges in grade from high-quality plastic fire clay, some of which is super-duty refractory grade, to impure red-burning pottery clays. The zone of clay beds in the vicinity of Tesla is about 400 feet thick (Huey, 1948, p. 34).

Clay production began during the waning years of coal mining in this area and continued intermittently through the turn of the century to the present time. The close association of coal and clay permitted removal of the clay through the old coal workings; but, when all the readily available clay was exhausted, further development work proved economically unfeasible. Although the clay is superior to many types being mined in California, the steeply dipping beds requires underground mining. Hence very little clay has been mined in the Tesla area. A large scale development of the Tesla deposits has been delayed by the presence of the large, easily mined deposits of similar clays elsewhere in California.



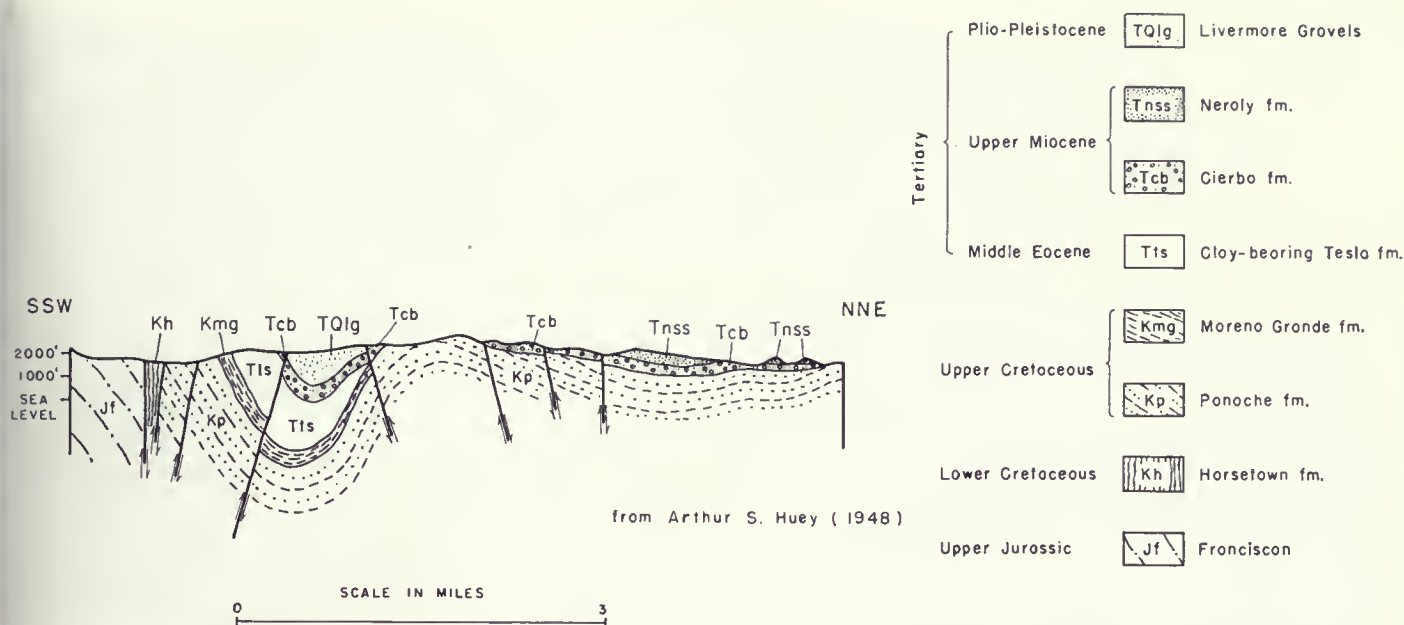


FIGURE 6. Geologic section through Tesla area, Alameda County.

#### Common Clay Deposits

Large tonnages of alluvial or common clay are abundantly distributed throughout the state. However, only near the centers of population, where structural clay products are in demand, have these deposits been worked on a large scale. In the Los Angeles area are about 60 clay pits in Recent alluvium. About sixteen of these pits have been operated in recent years. The San Francisco Bay area is supplied with common clay from shales of the Upper Jurassic Franciscan formation and from Recent alluvium, notably from the Niles alluvial cone in western Alameda County. Nearly every county in California has produced common clay in the past.

The Mojave Desert regions of Kern and Los Angeles Counties have yielded clay material from playa lakes that is used in oil-well drilling mud. The material is composed of illite, fine sand and chlorite. Swelling bentonite is added to the clay material to form a slurry that will withstand gas, oil, and water pressure during drilling. Principal production has come from Rogers, Buckhorn, and Muroc dry lakes.

#### Bentonite Deposits

Bentonite deposits are irregularly distributed throughout the southern half of California, and are associated with rocks that range in age from Paleozoic to Recent. Most of them are Tertiary in age. Thirty-two bentonite-bearing localities have been reported, most of them in San Bernardino, Inyo, Kern, and Ventura Counties. Seven of these deposits are being actively mined and intermittent production has been reported from nine others.

At the southern end of the Owens Valley, east of Olancha, the Sierra Talc and Clay Company mines non-swelling bentonite from the Calearth deposit. The clay averages about 16 feet in thickness, strikes N. 70°-85° E., and dips 10°-12° N. (Norman and Stewart, 1951, p. 98). The deposit is overlain by 10 to 20 feet of late Tertiary

or Pleistocene basalt. The dip of the clay beds and the volcanic cap necessitate underground mining of the greater portion of the deposit. Room-and-pillar type of mining is employed. The clay is believed to be derived from tuff beds that have been altered by hypogene solutions. The deposit is California's principal source of adsorbent clay. The clay is naturally adsorbent, but is further treated (activated) before use.

In southern San Benito County, a bentonite-bearing zone crops out for 12 miles along the southwest flank of the Vallecitos syncline. This zone, which contains both swelling and non-swelling bentonite, is near the base of the Kreyenhagen formation (Eocene) which is underlain by the middle Eocene Domingue (Yokut) formation and overlain by the Temblor formation (middle Miocene). The bentonite beds, of which there are at least four, are steeply dipping and each is about 50 feet thick. Only one thin bed of bentonite has been noted on the northeast flank of the syncline. The clay has been mined by open pit methods (C. W. Jennings, personal communication, 1956).

Bentonite also has been mined at several other localities in California, including Death Valley Junction, Tecopa and Kearsarge in Inyo County; near Johannesburg, San Bernardino County; near McKittrick, Kern County; and at Otay in San Diego County.

At Hector, in central San Bernardino County, is a deposit of hectorite, a unique, high-magnesia, low-silica, swelling bentonite which contains about one percent lithium. Hectorite, although differing in chemical composition from Wyoming bentonite, has similar physical properties. The clay is thought to be derived from a basic tuff or flow and lies in a sequence of folded and faulted lake beds of probable late Tertiary or Quaternary age. The lake beds are unconformably overlain by basalt, probably of Recent age, which originated from the nearby Mount Pisgah volcano. The Baroid Sales Division, National Lead Company and the Inerte Company op-





FIGURE 7. Little Antelope Valley clay deposit, Mono County. High-grade clay is being mined by Huntley Industrial Minerals, Inc. A, Present working face near east side of Little Antelope Valley. Most of the hill is underlain by clay. *Photo by Mary Hill.* B, Working face showing relic bedding of altered tuff.



erate adjacent underground mines in the Hector area. In the past, open pit mining was practiced. Most of the hectorite output has been used in oil well drilling muds. Since 1952, the Inerto Company has been beneficiating the hectorite in centricones and has sold the product for special uses in the pharmaceutical and beverage industries (Wright, et al., 1953, pp 157-160).

#### Other Deposits

The Hart area of the Castle Mountains in eastern San Bernardino County has yielded more than 200,000 tons of clay since mining operations began in the early 1920's. The clay material appears to consist at least partly of montmorillonite. The clay was formed by hydrothermal

alteration along steeply dipping fractures in Tertiary rhyolite. The altered zones are a few feet to several hundred feet wide and up to 1,000 feet long. The rhyolite strikes northward and dips 15 degrees to 30 degrees westward and is overlain by a thin veneer of alluvium. The clay contains masses of partly altered to nearly fresh rhyolite which need not be sorted out in the mining. The clay is mined by open pit methods. It is blasted and bulldozers are used to separate the ore from waste. When the clay is shipped vertical cuts are made through layered stockpiles to obtain a nearly uniform grade of material. The clay is used with talc in wall tile but a small amount goes into pottery and sanitary ware (Wright, et al., 1953, p. 156). Similar deposits of clay occur in Jawbone Canyon in Kern County.

In the southeastern part of Mono County, near Little Antelope Valley, a high-grade kaolin deposit is being mined by Huntley Industrial Minerals Incorporated. The clay appears to be derived from tuff by hydrothermal alteration along normal faults. Pleistocene lake beds and later volcanic ash, from a few feet to a few tens of feet thick, overlie the clay. The clay deposits is nearly flat-lying and it ranges in exposed thickness from a few feet to about twenty-five feet at the Huntley mine. The clay zone is discontinuously exposed throughout an area of about two square miles and is cut by numerous normal faults of small displacement. Open pit methods are used to mine the clay.

#### UTILIZATION AND CHARACTERISTICS OF INDUSTRIAL CLAYS

##### Physical Properties

From a commercial point of view, the more important physical properties of a clay material include plasticity,



green strength, dry strength, and drying shrinkage. These are referred to collectively as plastic properties. Clays possessing good plastic properties are termed "fat clays," and, conversely, clays lacking plasticity are called "lean clays." According to one definition, plasticity is that property which allows a material to be deformed without rupturing. The degree of deformation and the stress necessary to cause a material to deform are measures of the plasticity of a clay material. Deformation occurs by means of the movement of clay mineral particles with respect to each other, and takes place in the molecule-thin water film between the particles. Green strength is the strength of the clay material in a moistened, plastic state. Dry strength is the strength of the clay after it has been dried. Shrinkage is the loss in volume of a clay when it dries.

The plastic properties of clay material are functions of the ratio of clay minerals to other constituents, as well as the strength of the bonding forces between clay mineral particles and between them and the other constituents. The bonding forces in turn are determined by the strength of the electrostatic charges which exist at the surfaces of the clay mineral particles, and by the size and charge of the ions adsorbed on the particle surfaces. These electrostatic surface charges are inherent in the structure of the clay mineral.

Theoretically, a complete chemical and mineralogical analysis should be sufficient to predict the ceramic properties of a clay material; and, in practice, chemical analyses are useful in predicting and explaining observed firing properties. However, because of the lack of quantitative data that show relationship between the plastic properties and the clay mineral content, these properties can only be roughly predicted from a knowledge of the clay mineralogy.

These generalizations refer to clay material composed entirely of clay minerals. Impurities such as carbonaceous matter and perhaps free silica and iron oxide apparently affect the plastic properties of clay material, but in a way that is as yet not well understood.

Ceramic clays in the natural state are white, gray-white, yellow, brown, blue, green or red, or show gradations between these colors. They range in hardness from 1 to 2.5 and occur in granular to earthy masses and locally are scaly or platy. Specific gravity is variable depending on impurities; pure kaolinite ranges from 2.60 to 2.63. The melting of pure kaolinite begins at about 2820° F and is completed at about 3360° F, but impurities which are normally present lower these values. The fusing point ranges from about 1830° F for low-grade clays to as high as 2550° F for refractory clays.

#### Chemical Properties

Clays show a wide range in chemical composition. This can be attributed to a mixing of two or more clay minerals, the presence of mechanically admixed impurities, and absorption and adsorption of ions. The chemical properties of a clay also are influenced by the nature and amounts of impurities present.

Silica ( $\text{SiO}_2$ ) is present in most clays as sand grains or, in some deposits, in the opaline state. Silica is generally regarded as a refractory material in ceramic products, but only if it replaces stronger fluxes. In impure mixtures that contain a silica to clay ratio of less

than 4 to 1, the silica acts as a flux. The addition of silica to clay mixes helps to control shrinkage of the fired body. Silica promotes plasticity if it is in the colloidal state, but decreases plasticity if it is in the form of quartz. Silica-sand generally is considered deleterious in kaolin, but advantageous in common clay applications where shrinkage is an important factor. Some of the naturally occurring silica-rich clay is beneficiated to remove the silica or blended with other clays to arrive at the desired mix.

Finely divided iron-bearing minerals, such as limonite, hematite, siderite, and pyrite, are present in most clay materials. They discolor the fired products and also serve as a flux. White-burning clays contain less than 1 percent iron oxide, yellow and buff clays 1 to 4 percent, and red clays from 4 to 7 percent. If fired in a reducing atmosphere, a clay containing small quantities of iron will be tinged gray, and a clay containing more than 4 percent iron will fire dark gray or blue. In a reducing atmosphere ferrous oxide fires gray to blue and ferric oxide cream to red. The fluxing action of iron compounds reduces the vitrification temperature. Common clays, such as those used for brick, can be fired at low temperatures (about 1650° F) because they contain abundant fluxes, notably iron oxides. As refractory bricks, which are used to resist high temperatures, must be fired at high temperatures (about 2900° F), they must contain a low percentage of fluxes. Certain iron compounds on heating liberate gases, principally oxygen and carbon dioxide, which cause bloating in the finished body.

The calcium-bearing minerals, calcite, plagioclase and gypsum are generally considered to be deleterious in clays. However, when added in measured amounts, calcium carbonate is used as a flux. Calcium carbonate is generally injurious to ceramic bodies because it promotes bloating through the liberation of  $\text{CO}_2$ .

Compounds of sodium and potassium, which remain in partly decomposed feldspar, are common in most ceramic clays and are powerful fluxes. Fresh feldspar is added to some ceramic bodies; soda feldspars are more powerful fluxing agents than potassium feldspars as the former fuse at a lower temperature. Generally, these minerals are not pure, but each contains a small percentage of the other. Compounds of potash and/or soda are highly viscous at the fusing point and have a large temperature range between softening point and melting point. Material that has a high ratio of alumina to silica and low calcium content vitrifies at a higher temperature than material that has a low alumina-silica ratio and a high calcium content.

The salts  $\text{K}_2\text{SO}_4$ ,  $\text{Na}_2\text{SO}_4$ ,  $\text{CaSO}_4$ ,  $\text{MgSO}_4$ , and  $\text{KAl}(\text{SO}_4)_2$ , are common deleterious constituents of clay. They go into solution when the clay body is wet and deposit a white coating on the surface either during drying, firing, or in the wall.

Carbonaceous material is common in many clays and will give the raw clay a gray or black color. However, this material readily burns out on firing (900° F to 1650° F) and although it may cause difficulties in the firing process, it is not generally considered an injurious impurity.

The pH tests on kaolinite group minerals show a range of about 5 to 7, making them slightly acid as compared with montmorillonites which are generally alkaline.



Table 4. Preliminary field tests for clay.

Properties	Tests	Remarks and possible industrial applications (other properties being favorable)
<b>Physical properties</b>		
1. Odor-----	Breathe heavily on the sample	Clay will generally give a musty odor.
2. Color		
a. White, buff and gray	Observe natural color	Refractories; ceramic white-ware; heavy clay products; filtering; filler in rubber, paper and chemicals.
b. Reds, browns, greens and yellows	Observe natural color	Pigment; heavy clay products; drilling mud; decolorizer.
3. Hardness-----	Check pressure necessary to scratch the dry sample	Requires considerable pressure. Light color: High grade ceramic ware and refractories. Dark color: Heavy clay products and refractories. Hard clays tend to lack plasticity. Requires little pressure. Very light color; whitewares; paper; rubber; chemicals. Dark color: drilling mud; filler; some ceramic uses.
4. Texture-----	Observe presence of pisolitic or oolitic structures*	May indicate bauxite type clay that may be suitable as a refractory or as a source of alumina.
5. Plasticity and shrinkage	Rub moist clay between the fingers	Plastic clays can be worked into a definite shape and retain this shape after drying and without cracking.
6. Swelling-----	Slowly add finely divided clay to water	Certain bentonitic clays will swell many times their original volume, forming a gel. They may be used as a binder in foundry sands and in drilling muds, but are not in general, suitable for ceramics.
<b>Chemical properties</b>		
1. Impurities		
a. Iron-----	Heat a small sample of clay over a gas flame	Clays containing from 3 to 4 percent iron or more will turn red or brown and are not suitable for refractories or whitewares.
b. Calcium carbonate	Place a few drops of dilute hydrochloric acid on the clay sample	If the clay contains appreciable calcium carbonate, the sample will effervesce. Clay containing a high percentage of lime is not suitable for ceramic applications.
c. Soluble salts-----	Taste the clay and observe the outcrop in the field	A bitter taste may indicate alum or epsom salts. The presence of soluble salts can be detected on the outcrops as a white coating. Finished bricks made of clay high in these salts will have a white-washed appearance which is generally undesirable.
d. Sand-----	Check sampling by rubbing between the teeth	Sandy clays will feel gritty. If the clay is composed of 50 percent or more of sand it may be possible to use it directly for common brick. Some of the best quality fire clays contain high percentages of sand (90% or more in some cases) and still can be separated and marketed at a profit. Very light colored clays with very little sand are suitable for fine ceramic whitewares.

\* Spherical or ellipsoidal structures.

### Testing

Clays for use in whiteware, china and earthenware bodies are thoroughly tested because they must meet exacting service and esthetic requirements. The following procedure, taken from Brandt (1956, p. 145) briefly

summarizes the testing procedure followed in modern clay plants. Unfired test bars of the sample are checked for color and dry strength. During firing, the maturing range at different temperatures, and the amount of spotting impurities are noted. If this series of tests is favorable, a laboratory body is made of the material and the workability noted. The laboratory body is then fired and the casting rate, dry strength and shrinkage, fired strength and shrinkage, absorption and the fired color with different glazes is determined. Thermal shock and chipping tests provide data on glaze fit. If the laboratory study is promising then the material is tested in a jigger body and the same tests repeated. On passing these tests, a pilot batch is tried in the plant under rigid control and the resulting ware carefully checked for appearance, fired color, absorption, glaze fit, glaze blistering and chipping resistance.

In addition, clay to be used in tile bodies is closely checked for cleanliness, pressing characteristics and wet and dry strength. Post-firing tests include shrinkage, warpage, wedging, glaze color, autoclave resistance, thermal shock resistance, modulus of rupture, adsorption and cutting characteristics.

The refractoriness of a clay is determined by the Pyrometric Cone Equivalent test, which is one of the most widely used in the ceramic industry. The P.C.E. value is based on the fusion point of the clay sample tested under a specific heating schedule and compared to the fusion points of cones made from standard clay. Test procedures have been worked out by both the Orton Foundation and American Society for Testing Materials. According to the cone values obtained with P.C.E. tests a given clay can be classified as to its relative heat duty (table 5). P.C.E. values are also used as an index to the impurities which invariably affect the fusion point (Lohman, 1956, p. 151). Refractory clays are further tested for their iron content. A clay with a P.C.E. as high as cone 35 may be wholly unusable because of objectionable color.

Table 5. P. C. E. classification of refractory clays.

Heat duty	Fusion point*		
	P. C. E.	°C	°F
Super-----	33 plus	1745	3173
High-----	31-32	1680	3056
Medium-----	29-30	1640	2984
Low-----	19-28	1515	2759

\* At a temperature increase of 100° C. per hour.

As structural clay is used mostly in common and face brick, roof tile, floor tile and sewer pipe, firing color is perhaps the most important property. Dry and fired shrinkage is determined as is the saturation co-efficient on both the raw clay and the clay mixes. The testing of drying characteristics, although somewhat empirical, gives a relative evaluation of the color and cracking properties. Low strength and excessive loss in handling is expected of ware with a low modulus of rupture and therefore this property is generally tested. In addition, sewer pipe is tested for hydrostatic resistance and permeability.







Table 6. *California industrial clays.*

Principal commercial types	Principal mineral or minerals	Origio	Geologic age of principal deposits	Significant characteristics and chemical composition	Significant physical characteristics	P.C.E.*	Fired color	Principal areas or counties	Industrial applications
<b>Ceramic Clays</b>									
I. Fire clay	Kaolinite group	Residual and sedimentary (some deposits derived by hydrothermal alteration)	Paleocene Eocene	Principally silica (40-55%) and alumina (20-45%).	Highly refractory; generally plastic	19-35	White to red	Ione (Amador Co.) Alberhill (Orange & Riverside Co.'s), Lincoln (Placer Co.)	Fire brick, ladle brick, fire clay mortar, drain tile, face tile, pottery.
II. Kaolin (China clay)	Kaolinite group	Residual and sedimentary (some deposits derived from hydrothermal alteration).	Paleocene Eocene	Free from iron and alkalis with total oxide impurities less than 3%. Often high in organic material.	Low plasticity	32-35	White	Ione (Amador Co.) Alberhill (Orange & Riverside Co.'s), Lincoln (Placer Co.)	Whitewares, refractories, filler in paint, rubber, and paper.
III. Ball clay	Kaolinite plus montmorillonite	Residual and sedimentary (some deposits derived from hydrothermal alteration)	Paleocene Eocene		High plasticity	up to 32	White to light cream	Minor production reported from Stanislaus Co.	Whitewares; generally mixed with other clays to increase strength, bonding, and plastic properties.
IV. Miscellaneous clay	Kaolinite and illite	Sedimentary (generally alluvial)	Mesozoic to Recent	Principally alumina and silica (high in ferric oxides and other fluxes).	Low heat resistance	up to 19	Red	Found in all California counties.	Heavy clay products, building brick, face brick, paving brick, drain tile, sewer pipe; source of silica and alumina in cement; rotary drilling mud.
<b>Bentonitic Clays (General)</b>									
I. Swelling bentonite	Montmorillonite, beidellite, and hectorite	Residual and sedimentary (most deposits derived from volcanic ash)	Late Tertiary to Recent	Principally alumina, silica, magnesia and lime.				Kern, San Bernardino, Inyo, San Benito and San Diego Counties.	Suspending agent, filtering, decolorizing, filling agent.
II. Non-swelling bentonite (Adsorbent clays)				High in Na, low in Ca	Swells, forms a gel or suspension; high plasticity; non-activatable.			Hector (San Bernardino Co.), Death Valley Junction (Inyo Co.), Vallecitos (San Benito Co.), Randsberg (Kern Co.).	Well drilling muds, binder in foundry sands, pharmaceuticals; and beverage clarification.
A. Naturally active (fullers earth)				High in Ca, low in Na; good decolorizers				Olancha (Inyo Co.), McKittrick (Kern Co.).	Filtering, filler, insecticide carrier, decolorizer.
B. Activatable (activated)								Teopas, Shoshone (Inyo Co.), Trea Pinos (San Benito Co.), Olney (San Diego Co.).	Filtering; decolorizer for waxes, resins and petroleum oils; catalyst.

\* Pyrometric cone equivalent (a measure of resistance to vitrification). P.C.E. of at least 33—super duty; of 31—high heat duty; of 29—intermediate heat duty; of 19—low heat duty.



also exhibit thixotropic properties and low viscosity in water solutions to give an even surface during the coating process.

Great care is exercised in freeing the clay to be used in paper from any traces of foreign matter such as sand or grit. Only a few thousandths of one percent by weight of material left on a 325-mesh sieve is tolerated. Preventive measures to reduce contamination are practiced by selective mining of only the purest grades of clay, transporting the clay in covered hopper cars, fine screening, wet and dry magnetic separation of impurities, and the use of stainless steel piping within the plant to reduce pipe scale contamination. The gritty material that reaches the coating roll will become imbedded in it and produce an uneven surface which will interfere with the printing. Most paper clays produced domestically must be bleached to produce a sufficiently white product. This is accomplished with hyposulfites of zinc or calcium. The bleached clay will give a brightness value of about 80 percent. This figure is determined from a brightness meter which compares the sample to a standard and gives the brightness value as a percentage of the standard. Paper clays range in pH from about 4 to 6 depending on the inherent pH of the crude clay and the pH of materials introduced during processing. Only a little of the clay produced in California has been used in paper. Past attempts to beneficiate California fire clay for paper applications proved to be economically unfeasible.

Kaolin used in rubber goods imparts stiffening and reinforcing properties and improves resistance to abrasion. It is used as a pigment in non-black goods and is added to molded rubber articles to reduce molding problems. Clay is used in rubber heels, soles, tiling, flooring, matting, insulated wire, gloves, bicycle tires, sponge, gaskets, toys, adhesives, butyl inner tubes and neoprene compounds. Such clay should be almost free of copper, manganese and iron oxides. Small amounts of titanium, calcium, sodium, magnesium and potassium oxides can be tolerated. Mica is detrimental in clay used in small extruded articles because it collects on the inner surface of the die. Rubber clay should pass 100 percent through a 100-mesh screen and 99.5 percent through a 300-mesh screen.

The use of kaolin in the ceramics industry is based primarily on its high refractory and white burning properties. Cone 34 kaolin is suitable for all refractory purposes; however, in many applications cone 32 clay is sufficiently refractory. Kaolin is not plastic enough to be used alone, but is mixed with ball clay. This improves workability but reduces heat resistance. Ceramic kaolin must be nearly free of alkalis, alkaline earths, excessive amounts of silica and iron oxide which act as fluxes and thus lower the refractory properties and discolor the fired product. It must be ground so that 98 percent of the clay will pass a 200-mesh screen. Kaolin to be used in ceramics is held to few industry-wide, standard specifications, but the American Ceramic Society has set up tentative standards and the American Society for Testing Materials has developed tests for finished refractory bodies. The specifications of kaolin used in ceramic wares are largely determined by the individual consumer in view of his specific requirements.

Kaolin is used in the manufacture of glazes, stoneware, high-grade tile, kiln furniture (saggers, pins, and stilts), art pottery, flower pots, firebrick, fireclay mortar, clay crucibles, glass refractories and in special applications in the steel industry. The numerous small art pottery and dinnerware manufacturers in the Los Angeles and San Francisco areas use kaolin from Tennessee and Kentucky. The clay mined from the Hart deposit in San Bernardino County, Little Antelope Valley deposit in Mono County, the Arnold and the Schoeppe deposits in Orange County are generally given a commercial classification of kaolin.

**Ball Clay.** Ball clay burns white or nearly so, is composed of kaolinite-group minerals, and possesses high bonding power and high plasticity. It shows a marked range in chemical and physical properties. Ball clay is similar to kaolin in chemical composition, but fires less white. A typical ball clay contains 40 to 48 percent silica, 32 to 36 percent alumina, less than 2 percent iron oxide, 1 percent lime and magnesia, and 3 percent potash and soda. Common impurities are pyrite, mica, and free silica and organic matter. Ball clay generally contains more alkali and iron than kaolin; a factor that limits its refractory properties. Quality ball clay will pass a 100-mesh screen and leave little residue on a 120 or 150 mesh screen. The strength of this type of clay is generally high, the modulus of rupture ranges from 150 to 500 psi and the tensile strength from 125 to 250 psi. Ball clay exhibits a high degree of dry shrinkage, and has a fired shrinkage of as much as 12 percent.

Ball clays are used in ceramic mixes primarily to provide high plasticity and binding power. Most white-ware, pottery and firebrick contain 6 percent to 45 percent of this type of clay. To a lesser degree ball clay is used in architectural terra cotta, kiln furniture, fire clay mortar, enameling, stoneware, glazing, and in the steel industry. Non-ceramic applications include fillers, chemicals and fertilizers; these uses are minor and account for only 2 or 3 percent of the ball clay produced domestically.

Although about 350,000 short tons of ball clay is produced in the United States each year, California yields only a few hundred tons which comes from the Sierra foothill area. Kentucky and Tennessee are the sources for most of the ball clay used in California.

**Fire Clay.** Fire clay is a heat resistant, plastic to non-plastic clay composed principally of kaolinite-group minerals and commonly associated with coal. Most clays with a P.C.E. of 19 or higher, and that are non-white burning, are considered fire clays. In the unburned state they generally are colored white, black, red, brown, yellow, gray, or blue, and some have a mottled texture. The fired color ranges from near-white to red. Fire clay characteristically is fine-grained enough to permit most of the particles to pass a 200-mesh screen. Quality fire clays are free from excessive grit. Specific gravity ranges from 2.6 to 2.75. Although not as plastic as ball clays, fire clays can generally be shaped. Certain non-plastic fire clays are called flint clay. The chemical compositions of fire clays show much variation.

In typical analyses, silica ranges from 46 percent to 81 percent; alumina 12 percent to 36 percent; iron oxide



.5 percent to 5 percent; lime .1 percent to 1 percent; magnesia .5 percent to 1 percent; soda plus potash 3 percent to 5 percent and water, 4 percent to 14.5 percent (Searle, 1950, p. 65). Quality fire clays should contain less than 2 percent each of lime, alkalis (some good quality clays may contain 5 percent alkalis), and titanium oxide. Most fire clays are richer in silica than are kaolins. Numerous impurities are commonly present, including: silica in the form of sand and in the colloidal and hydrated form, feldspars, hornblende, tourmaline, limonite, hematite, pyrite, calcite, gypsum, witherite, magnesite, mica, rutile, and carbonaceous material.

The use of fire clay is based principally on its refractory properties and the resistance of bodies made of fire clay to corrosion by spalling and abrasion. Fire clay is used mostly in the manufacture of fire brick and heavy clay products, which include: common brick, face brick, paving brick, drain tile, and sewer pipe. Considerable amounts go into high-grade tile, fire brick mortar, chemicals, stoneware, art pottery and flowerpots, architectural terra cotta, kiln furniture and foundry and steelwork applications. Minor uses include zinc retorts and condensers, whiteware, fillers and cement. The American Society for Testing Materials (Manual of ASTM Standards on Refractory Materials, 1943) has developed numerous tests and specifications for refractory applications of fire clay.

Most of the fire clay produced in the Ione and Lincoln areas is used in the manufacture of sewer pipe and other heavy clay products at plants at Stockton and Lincoln. Sewer pipe is made only by the large companies with plants located near Los Angeles and San Francisco. The greater part of the Alberhill clays mined near Los Angeles, are utilized locally in making heavy clay products principally at Corona, Los Nietos and Los Angeles. Part of the refractory fire clay mined in the Ione area is made into refractory brick at Ione, but most of it is shipped to Pittsburg near San Francisco for fabrication. Only a small amount of the fire clay produced in California is of sufficient purity to be used in whiteware.

The annual production of fire clay in the United States amounts to nearly 12 million short tons of which California yields nearly 500,000 short tons.

*Miscellaneous Clay (Common Clay).* "Miscellaneous clay" is a broad classification that includes many types of impure clay materials. Raw materials come principally from shales and alluvium and are composed of various proportions of clay minerals, sand, silt, weathered rock and mineral fragments and organic matter. Most miscellaneous clays are brown to light tan in the raw state. Their heterogeneity is reflected in a wide range of chemical and physical properties. Actually, a few materials in miscellaneous clays can be classed as impurities, as the useful properties of such clays stem not only from the clay mineral content, but also from other minerals and materials present. For example, sand and iron oxide, which act as impurities in some other clays, are desirable ingredients in most miscellaneous clays. The sand reduces plasticity and shrinkage and the iron oxide causes a red fired color. The grains range from clay size particles to pebbles, and show a marked range in size distribution from place to place in a given area or deposit. Soluble salts, principally sulfates of potassium, sodium,

calcium and magnesium and alkali chlorides, alkali carbonates and alkaline earth carbonates, may be present in these clays and lead to objectionable color changes on the surface of the finished ware. Although the effect of these salts usually can be controlled, their presence in clay is not desirable. Limestone fragments, unless finely divided, are detrimental in clay used in fired products as they expand in the clay body and react with mortar.

The United States produces about 27 million tons of miscellaneous clay yearly of which California yields about 2 million tons. Heavy clay products including common brick, face brick, paving brick, drain tile and sewer pipe, utilize more miscellaneous clay than all other uses combined. Large tonnages are used by the Portland Cement industry as a source of alumina and silica. Other important uses are in high grade tile, fire brick, rotary drilling mud, foundry and steel work, art pottery and flowerpots. Minor amounts go into fertilizers, fire clay mortar, insecticides, and paint.

Brick clay must be easily molded, burn at a low temperature (1800° to 1900° F.) and develop hardness and strength with minimum cracking and warping. A high sand content is desirable to limit shrinkage. A highly plastic raw clay may require the addition of sand to reduce the plasticity and shrinkage. Linear shrinkage ranges from 0 percent to about 13 percent. Modulus of rupture varies from 50 psi to 1500 psi and the tensile strength from about 60 psi to 500 psi. Maximum particle size is generally not greater than 4 mesh. About 4 tons of clay are required to make a thousand standard 9-inch bricks. The chemical analysis of brick clay is sometimes useful in determining the fired color and the fusibility. The wide variation in composition of brick clays is illustrated by the following ranges in chemical constituents taken from nine analyses reported by Ries (1927, p. 350):

	Range
Silica -----	18.62-88.71%
Alumina -----	3.23-20.62
Ferric iron -----	1.26- 6.55
Lime -----	.56-41.30
Magnesia -----	.11- 6.01
Potash -----	trace- 5.98
Soda -----	trace- 1.86

*Modified after Ries (1927)*

Face brick requires a higher grade clay than common brick to assure a uniform fired color, lack of warping, low absorption, and low content of soluble salts. The fired color ranges from red to buff. In chemical composition it shows less variation than common brick.

Sewer pipe clay must yield a vitreous product of high strength and low porosity and hence requires a higher grade clay than that used in common brick. Common clay, which lowers the firing temperature, is mixed with refractory clay in proportions that yield a product that is free from warping or cracking and one that will take a salt glaze. Sewer pipe clay is ground to the 4 to 20 mesh size range.

Miscellaneous clays used in cement should contain less than 1 percent magnesia and 1 percent total alkalis (soda and potash). A high content of iron and titanium oxides may cause pigmentation in the production of white cement. However, iron is added to some types of cement. Clay used in cement amounts to about 25 per-



cent of the mix; the balance generally being calcined limestone (see section on cement in this volume).

Miscellaneous clays are mined and used principally in the large population centers of Los Angeles and San Francisco. Common brick and other structural products made from these clays are in demand for home and industrial buildings. Production comes from numerous small plants as well as from the large integrated plants. Nearly every large town in the San Joaquin-Sacramento Valley, for example, has a local manufacturer of common brick.

**Bentonite.** Bentonite is a rock name for clay material composed principally of montmorillonite-group minerals. When mixed with water certain varieties (swelling bentonite) will expand many times their original volume, while other varieties (non-swelling bentonite) show little change in volume. Certain non-swelling bentonites when treated with acid develop adsorptive properties making them useful as decolorizing agents. Fullers earth, which is a bentonite, has natural adsorptive properties and therefore can be used without acid treatment. Although activated clays are more expensive than fullers earth, they have about four times the adsorptive power.

Bentonite shows a wide range of colors, but is generally cream to olive green and sometimes white, yellow, pink, dark brown, or black. Hardness varies with the water content; dry bentonite has a hardness of about 2. Most bentonite is dull, powdery, massive or earthy. Some bentonites have a roughly conchoidal or platy fracture, but others show no apparent fracture. Pure bentonites have a specific gravity of about 2.

Swelling types, when water-saturated, have a waxy luster and much the same consistency as soap. Bentonitic gels exhibit thixotropic properties in that they are fluid when shaken and become stiff on standing. Clay minerals of the montmorillonite group are more plastic, when mixed with an optimum amount of water, than those of the illite and kaolinite groups. The high plasticity of montmorillonite stems largely from the weak interparticle bonds which allows water to penetrate between the particles—a property common to the swelling bentonite. The better grades ordinarily will swell 12 to 15 times their original volume and some swell as much as 30 times. The swelling and plastic properties appear to be related to the presence of exchangeable sodium and calcium ions. Swelling clays generally contain more sodium whereas calcium seems to be the more abundant in non-swelling varieties. Common mineral impurities include feldspar, biotite, gypsum, quartz, pyroxene, and zircon.

Bentonite is used principally in oil-well drilling muds, as a filtering or decolorizing agent, and as a binder in the foundry and steel industries. It is also used in chemicals, insecticides, concrete, dam sealing and numerous other minor applications.

The petroleum industry consumes the largest tonnages of bentonite principally as an additive in oil-well drilling mud. Its gel-forming and thixotropic properties, when it is mixed with water, make it an excellent circulating medium for carrying drill cuttings. Bentonite also prevents the cuttings from settling out of the mud when drilling is stopped. Bentonite insulates the hole from drill fluid seepage into the surrounding rock, and in

many instances prevents the walls from sloughing, making it unnecessary to use many thousands of feet of expensive casing.

Non-swelling bentonite can be treated with acid to produce a clay with adsorptive or decolorizing properties. Activated clays will remove objectionable color from petroleum products and will act as a catalyst during the cracking process. Bentonite can be used to remove sulfur, nitrogen, sulfuric and sulfonic acids, oxygenated compounds and pitchy materials from petroleum (Lamar 1953, p. 328).

Colorants in vegetable, animal and marine oils, as well as other deleterious substances, such as chlorophyll and peroxides in vegetable oils, can be removed effectively by activated bentonite.

The foundry industry utilizes bentonite as a binder in foundry sands. Foundry sand-bentonite mixtures are tested for green, dry, and hot compression strength, moisture, grain size, and green permeability. Plasticity or bonding power is the most critical property and is related to the base exchange capacity of the clay. Specifications can be found in the "Foundry-sand testing handbook" published by the American Foundrymen's Association (1945).

High-grade swelling bentonites are used for beverage clarification and stabilization in the Los Angeles and San Francisco areas. Special types are sold outside the state for use in pharmaceutical products. Bentonite mined in San Benito and Inyo Counties has been used locally for sealing canals and earth-filled dams. Small tonnages of bentonite from the Mojave Desert have been used for a binder in foundry sands but most of this type of clay is shipped into California and used principally in the Los Angeles and San Francisco areas. Large tonnages of high-quality swelling bentonite are brought into California from Wyoming for use in oil well drilling mud. California's annual production amounts to about 2500 short tons of bentonite. Total U. S. production is nearly 1½ million short tons per year.

**Fullers Earth.** Fullers earth, a non-swelling, naturally adsorptive bentonite, consists mostly of montmorillonite-group minerals, but kaolinite and illite are commonly present. Impurities include hydrous silica, calcite, volcanic ash and sand. Fullers earth is commonly

Table 7. Chemical analyses of bentonite and fullers earth from deposits in California. Analyses 1-3 from Lamar (1953, p. 320), 4-5 from Ross and Henricks (1945, p. 35).

	(1) Percent	(2) Percent	(3) Percent	(4*) Percent	(5) Percent
SiO <sub>2</sub> -----	58.63	61.50	45.62	55.86	50.30
Al <sub>2</sub> O <sub>3</sub> -----	12.76	14.37	8.43	.13	15.96
Fe <sub>2</sub> O <sub>3</sub> -----	5.92	1.36	0.57	.03	.86
MnO <sub>2</sub> -----	0.03	trace	trace	none	--
MgO-----	3.39	4.26	21.89	25.03	6.53
CaO-----	1.21	0.15	3.14	trace	1.24
K <sub>2</sub> O-----	1.65	0.42	0.67	.10	.45
Na <sub>2</sub> O-----	0.91	0.62	0.72	2.68	1.19
TiO <sub>2</sub> -----	0.47	0.08	0.19	none	--
H <sub>2</sub> O-----	9.33	10.11	11.93	9.90	23.61
H <sub>2</sub> O+-----	5.74	6.80	5.27	2.24	

(1) Fullers earth, Calearth deposit, Inyo County.

(2) Fullers earth, Muroc deposit, Kern County.

(3) Saponite, Death Valley Junction, Inyo County.

(4) Hectorite, Hector, San Bernardino County.

(5) Montmorillonite, Otay, San Diego County.

\* LiO—1.05 percent; F—5.96 percent.





FIGURE 9. Calcearth fullers earth deposit near Olancho, Inyo County. *Photo by Charles W. Jennings.*

pale green, gray, brown, cream or buff. It is generally non-plastic but some types are semi-plastic.

The alumina-silica ratio of adsorbent clay ranges from 1:2 to 1:8 (Lamar, 1953, p. 303). A high ratio commonly indicates high adsorptive capacity. Apparent acidity in water also is used as an index to adsorptive capacity if the clay contains no soluble salts. Some clays require from 10 to 150 cc. of 0.1N NaOH to neutralize a 100 gram sample (Lamar, 1953, p. 303). The adsorptive ability of the clay removes bases from solution (base exchange), resulting in a lowering of pH. Adsorptive capacity is both a chemical and physical process. Although this process is imperfectly understood, the material being adsorbed apparently undergoes a chemical change at the surface of the clay particle and becomes tightly held by both a physical and chemical bond. As a measure of adsorptive capacity Mantell (1945, p. 53) estimates that one cubic foot of fullers earth could adsorb 0.6 pounds of lime.

Fullers earth is used principally as a decolorizer in the bleaching of petroleum products and as a catalyst in vegetable, animal and marine oils, and in oil-well drilling mud, filtering, insecticides and fungicide carriers, fillers, water softeners, ceramics, cements, fertilizers, molding sands and adsorbent carbon.

Tests and specifications for the different uses of fullers earth are largely empirical. In general, a clay will be tested for adsorptive power in relation to the type of material being treated. A clay exhibiting high ad-

sorptive power with one type of oil may be wholly unsuitable for another type. Fullers earth ordinarily is ground to three sizes: material passing 15 mesh and retained on 30 mesh, through 30 on 60 mesh and through 60 on 80 mesh. Freedom from fines, which would inhibit percolation, also is specified. Other desirable properties are minimum adsorption of oil by the clay, reusability of spent clay after suitable treatment, and freedom from odor or taste that may be introduced into the oil (Ladoo and Myers, 1951, p. 238). A recent detailed discussion of fullers earth and other materials used as catalysts in petroleum cracking is given by Milliken, et al. (1955, p. 314). Common substitutes for fullers earth in bleaching oils are activated bauxite, synthetic magnesium silicate and activated bentonite. Diatomite competes in filter applications.

The fullers earth mined in the Owens Valley region is used in adsorbent applications for deodorizing and decolorizing mineral and vegetable oils in the Los Angeles and San Francisco areas. In recent years about 10,000 short tons of fullers earth is produced annually in California. California imports large tonnages of bentonitic clays from deposits in Nevada and Arizona. Total United States production amounts to about one-half million short tons.

#### Mining Methods and Treatment

Clay is mined in the United States by four principal methods: open pit, underground, hydraulicking and dredging. Open pit mining is the most widely used. If



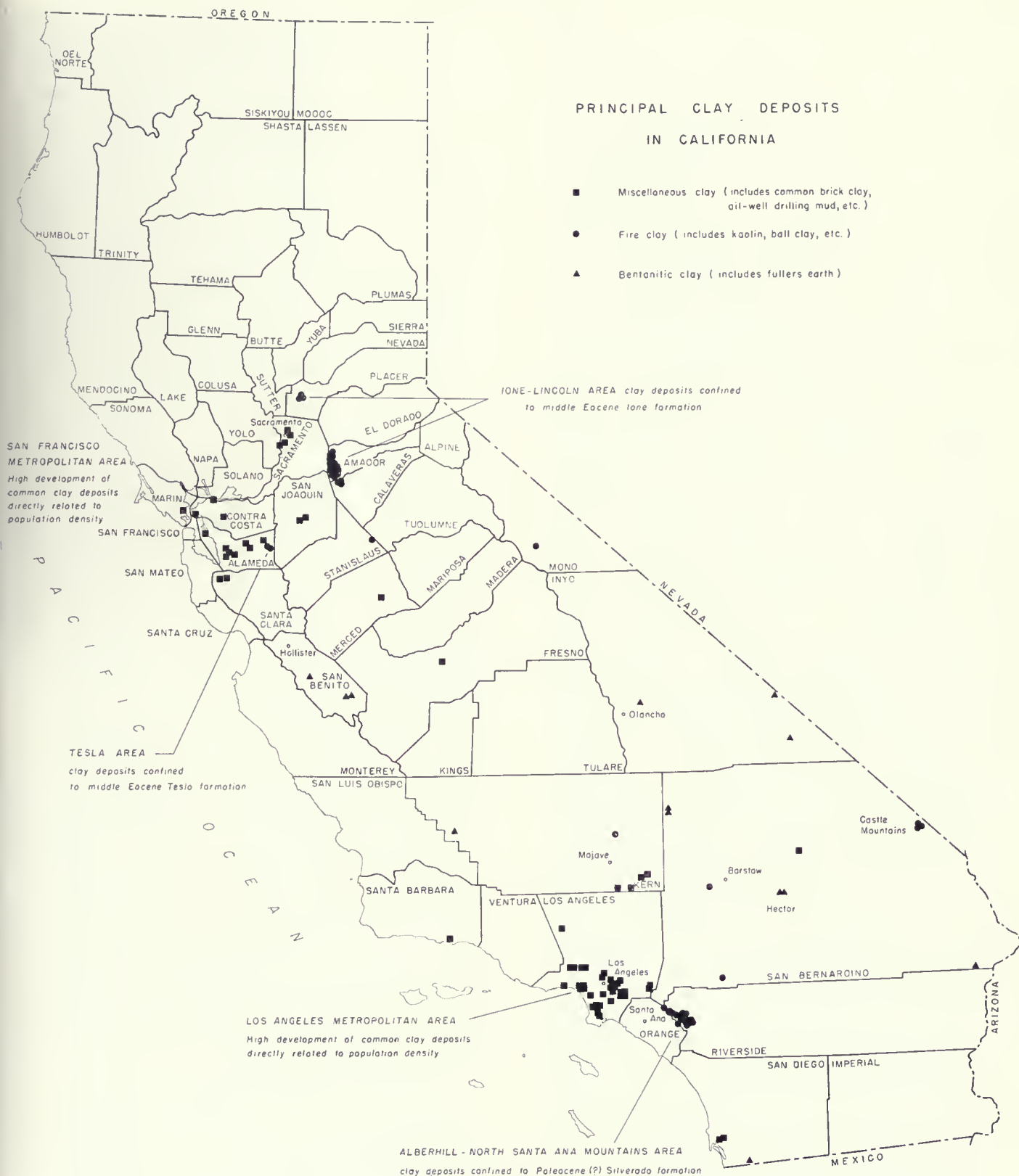


FIGURE 10.



the clay is of sufficient value and the cost of removing overburden becomes excessive, underground mining is practiced. Only under special conditions is clay recovered by hydraulicking or dredging.

In California, open pit methods are used almost exclusively. The overburden is stripped off and the clay removed by dragline buckets, power shovels, tractor shovels, bulldozers, or scrapers. Skip loaders and other power loaders transfer the clay to bins or stockpiles for storage or directly into trucks where it is moved to the railroad or directly to the plant. In mining common clay, little or no overburden can be moved. In mining some deposits of high-grade ceramic clay, tens of feet of overburden are removed to reach a relatively thin clay bed. In California, the ratio of thickness of overburden to thickness of clay may be as high as 7.5 to 1. In the Ione area of Amador County this ratio is generally in the range of 1:15. The cost of mining clay varies in different parts of the state, according to the type of mining method used, the type of equipment available and the size of the operation. To strip and mine fire clay, by means of the most modern (1956) techniques, costs about 25 cents a short ton in the Ione area. In many deposits different beds are selectively mined by benching. As clay plants in California commonly blend clays from different deposits or different clays from the same deposit, great care is exercised in keeping the various types separated during the mining operation. In some operations, hand methods are used. Seldom is blasting necessary in California mines; when needed, 25 percent or 40 percent dynamite is used.

The larger clay companies conduct organized drilling programs prior to and during the mining operations. Such data as thickness of overburden, thickness of clay, dip of the clay bed or beds, quality and quantity of clay and limits of economic recovery often can be determined. Churn drills or soil augers are commonly used for this work.

Underground as well as open pit mining has been practiced at the hectorite mines in San Bernardino County, at the Calearth fullers earth deposit in Inyo County, and at the Claymont mines in Orange County. Until the mid-1940's clay was recovered underground at the Edwin mine near Ione, Amador County.

Few clays are marketed to the consumer without some type of previous treatment. This may consist only of grinding, as with common clay, or may involve elaborate processing such as the removal of impurities in the preparation of paper clay. The general procedure for the treatment of high-grade ceramic clays includes drying, grinding and screening. If such materials as quartz, mica, and feldspar are to be removed, a slurry of clay and water is passed through inclined troughs where the coarser material is removed. Mica is recovered in longer, more gently inclined troughs and on screens. The slurry is sent to settling tanks where the clay is removed as a thick clay-water mixture. The suspension is transferred to an agitator, then filtered and the filter cake dried. The most modern plants employ vibrating screens, concentrating tables and jigs, classifiers, and flotation techniques to remove impurities. Deflocculating agents commonly are added to speed the settling of the clay. Bentonitic clays are crushed, watered, dried, ground and air classified. High-grade types are put through centrifuges

to remove calcite, dolomite and other impurities. Activated clays are treated with acid to improve their adsorptive capacity and some naturally active fullers earth may also be improved by this method.

One plant in California is separating and marketing both sand and clay from a deposit in the Ione formation and a second plant is nearing completion. The Pacific Clay Products Company sand plant at Camanche, Calaveras County, plans to recover sand and clay from the upper member (?) of the Ione formation. Although the company is still experimenting with equipment, the following flow of material through the plant will be generally followed: A sand-clay slurry is pumped to the plant from adjacent pits where a portion of the clay is removed by desliming cones. The slurry is pumped to attrition scrubbers and through screens to a classifier where additional clay and fines are removed. It is then passed through flotation cells, where the heavy minerals are removed by a second classifier and in which the third clay separation is accomplished. The clay-free sand slurry is then filtered, dried, and iron is removed by magnetic separators. Clay comprises only a small portion of the processed material.

A similar plant for the simultaneous recovery of sand and clay is being operated jointly by Owens-Illinois Glass Company and Gladding, McBean and Company near Ione in Amador County. However, here the sand and clay fractions are more nearly equal, as the crude mixture contains about 60 percent sand and 40 percent clay.

#### Markets and Prices

Most of the commercial clay deposits in California are owned or leased by the companies that manufacture clay products. This is especially true of the lower- and intermediate-grade clays used in common ceramic products. It is less true for the high grade-clays mined in limited amounts for specialized applications.

The independent owner of a clay deposit has the choice of leasing or selling his property or mining and marketing the clay himself. When a property is leased or sold the price is negotiated on the basis of nearness to transportation and market; mining cost; quality, amount and type of clay; uniformity of deposit, and on the immediate and future needs of the purchasing company. When a property is leased, contracts often call for a set yearly payment and a royalty on each ton produced. In mining a deposit, the small producer is faced with the problem of selling his clay to a highly competitive and nearly captive market without enjoying the economies of large-scale production. Unless the clay in a given deposit has unique properties useful in some specialized industrial process or is of extremely high quality, it will ordinarily be difficult for an individual to develop and market.

Transportation cost is a critical factor in clay production where the point of consumption is not near the deposit. Many clay deposits in California are uneconomic because of their inaccessibility to low-cost transportation. The distance a clay can be transported is related directly to its value. For example, common clay used for brick must be mined and fabricated at the same location whereas fine English china clay can be shipped throughout the world. In California, the clay producer must also consider the distance the finished product must be



shipped to market. The Los Angeles and San Francisco Bay areas are the principal marketing centers and clay plants are generally located in the immediate vicinity.

The transportation cost for a typical large scale clay operation in California is about 4 cents per ton-mile, including loading and unloading. Rail costs are between 1 and 2 cents per ton-mile exclusive of loading and unloading. In 1956, the freight rate to ship Georgia kaolin by rail to either Los Angeles or San Francisco was about \$20 a short ton in 40 ton lots. Ball clay from Kentucky is shipped for about \$17 per short ton in 50-ton lots.

Mine owners who wish to sell their clay or to lease or sell their deposit should send representative samples to the principal clay companies for consideration. Included with the samples should be such information as: location, size, and uniformity of the deposit; approximate dip of the clay bed; thickness of overburden; transportation facilities, including distance to nearest railhead, and condition of roads; and proof of ownership, such as a copy of the land deed, claim, or lease.

The unit value as well as the total value of clay produced in California has been increasing since 1949. California's ceramic industry still depends in large part on imports of high-grade clays from other states. Although the state has ample supplies of miscellaneous clays, most fire clays, and certain types of high grade bentonitic clays, there is a need to locate and develop local sources of high refractory, ball and bentonitic clays. The relatively high cost of shipping these out-of-state clays into California supports their high price. Although most of the clay mined in California is used within the state, some types, notably fullers earth, are shipped to other states and to other countries. As California is the only known source of hectorite, this clay is shipped as far as the East Coast.

In recent years the value of clay in the Ione area has ranged between \$2 and \$5 a ton at the mine. Selected types bring more. The average for all clays mined in this area is slightly more than \$2 a ton. The value of fire clay produced at Lincoln in Placer County is about \$2 a ton. Most of the fire clay mined in the Alberhill area of Riverside and Orange Counties ranges in value from about \$2 to a little less than \$10 a ton; special types bring as much as \$25 a ton. Miscellaneous clays mined in the Alberhill area are valued at about \$3 a ton and kaolin at about \$17 a ton. Miscellaneous clays bring about \$1 a ton in the Los Angeles area and from \$0.50 to \$1.50 per ton in the San Francisco Bay area. Rotary drilling muds that are produced in the desert areas are valued at about \$4 a ton. Bentonite is sold between \$10 and \$50 a ton; one type after processing brings over \$200 a ton. Fullers earth varies in price between \$25 and \$45 a ton. Activated bentonite ranges from about \$45 to about \$80 per ton (Lamar, 1953, p. 325).

In the United States kaolin is sold in carlots; select types are crushed, pulverized, washed, purified or air floated and marketed in bags. Ball clay is sold in bulk or crude, air floated, shredded or pulverized in bags. Fire clay is marketed in carlots, bulk and in bags. Miscellaneous clays are generally sold in carlots. Bentonite comes dried, crushed in bulk and pulverized to 200 mesh in bags. Fullers earth is marketed in four particle size ranges: 14 to 30 mesh, 30 to 60 mesh, 100 mesh up, and 200 mesh up, in bulk and in bags.

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## COAL

BY CHARLES W. JENNINGS

Coal was first mined in California in 1855, and the peak annual output of 236,950 long tons was reached in 1880. Since 1910, production has been much lower, principally because of competition from petroleum and natural gas and the depletion of much of the early recovered coal. The total production of coal in California through 1954 was 5,290,000 tons valued at \$23,600,000. Compared to the total annual production of coal in the United States, California's yield is of little national significance. The California coal industry, however, is of considerable interest historically, and recent developments in the extraction of waxes and pigments from lignitic coals have led to a partial revival of the industry in the state. In the period 1949-55, about 3,000 tons of lignite were mined annually. Current interest in uranium-bearing carbonaceous rocks and raw materials for synthetic liquid fuels has initiated a re-examination of California's lignitic coals.

### GEOLOGICAL OCCURRENCE

Coal is a carbonaceous rock formed by the decomposition of plant material by various biochemical processes. The plant material is first converted to peat, then compacted by burial, and finally metamorphosed into coal. The formation of coal begins in swamps when plants die and are covered by water. The water excludes oxygen and prevents rapid decay of the material allowing it to accumulate and develop into peat. The weight of more vegetation falling on the peat helps to compress and solidify it, as does the weight of water when the deposit sinks below a lake or sea, as has often happened. At the end of coal-forming periods, swamps remain flooded for a long time and sediments are deposited in thick beds over the peat. This further compresses it and starts the coalification process. The transformation from vegetation to rock is slow and requires geologic ages to complete. Lignite is the first coal to form from peat, and as the process continues, coals of higher rank are developed, ranging from lignite through sub-bituminous, bituminous, to anthracite. In general, the older coal beds contain higher-rank coal than the younger beds. Most of the coal in the United States was formed during the Carboniferous and Cretaceous periods.

### LOCALITIES IN CALIFORNIA

Coal occurrences have been reported in 43 counties in California, but only at a few locations is the coal of sufficient quantity and quality to warrant consideration for commercial development. The coal deposits in this state occur mostly in Paleocene, Eocene, and Miocene formations, but in Trinity County coal deposits occur in Cretaceous beds. The coal characteristically is interlayered in shale, sandstone, clay and conglomerate, forming distinct layers, or seams. Some of the lignite deposits in California contain lenses as much as 24 feet thick. This compares favorably with the thickness of coal beds in other parts of the world, for although coal beds are known to be as thick as 100 feet, they are rarely over 8 or 10 feet thick (Ries, 1937). However, most of the coal beds in California are apparently of limited extent and

few seams have been traced more than a few square miles. By comparison, coal fields in eastern United States and in the Rocky Mountains are known to underlie hundreds and even thousands of square miles.

Records and reports of production are fragmentary and incomplete. In many places, the coal beds have not been mapped and their extent is unknown, hence recoverable coal reserves of the state remain undetermined.

The principal coal mines in California have been those at Mt. Diablo, Contra Costa County; Corral Hollow, Alameda County; Stone Canyon, Monterey County; Alberhill, Riverside County; and Ione, Amador County. In the Coast Ranges most of the coal-bearing formations dip steeply and are commonly offset by faulting. In the foothills of the Sierra Nevada and in the Peninsular Ranges the coal beds dip gently or are horizontal, but even within small areas the thickness and character of the coal are most irregular.

*Mt. Diablo District, Contra Costa County.* The coal mines on the northeast slopes of Mt. Diablo, east of San Francisco Bay, were first worked in 1855. These mines were destined to become the principal sources of coal in California, and by 1859 they were supplying much of the domestic coal used in San Francisco. In 1870, more than 1,000 men were employed at the Mt. Diablo mines, and Nortonville, Somersville, and Stewartsville existed primarily as mining communities. The production of the Mt. Diablo properties declined rapidly about the turn of the century and ceased in 1902. The abandonment of the coal mines was attributable to rising mining costs as the workings increased in depth, and to the competition with cheaper coal from outside the state. Although production statistics are incomplete, about 3,500,000 tons of coal are estimated to have been taken from this district (Davis, 1951, p. 590).

The coal beds in the Mt. Diablo district are in the Domingine formation (middle Eocene), and crop out around the northern slopes of Mt. Diablo. They are associated with white sandstone and impure coaly beds essentially the same in character and age as the coal-sand-clay formations in the Sierran foothills. Many geologists consider the Mt. Diablo coal measures to be part of the middle Eocene Ione formation of the Sierra Nevada, but the two rock groups cannot be traced continuously across the Great Valley because of the vast thickness of alluvial fill. The coal formation in the Mt. Diablo district covers a belt no more than  $2\frac{1}{2}$  miles long, curvilinear in outline and convex northward (Smith, 1902, p. 498). The two principal coal seams are the Clark and the Black Diamond which dip  $20^{\circ}$ - $30^{\circ}$  N. E. The Clark seam ranges from  $1\frac{1}{2}$  to  $4\frac{1}{2}$  feet in thickness, and is generally free of any interstratified shale or other undesirable material. The Clark vein proved the more profitable, because it occurred within stable sandstone walls which did not require expensive timbering. The Black Diamond seam, which occurs about 375 feet stratigraphically below the Clark seam, ranges from 6 to 18 feet in thickness, but contains much interstratified claystone and sandstone. The seam lies between weak walls



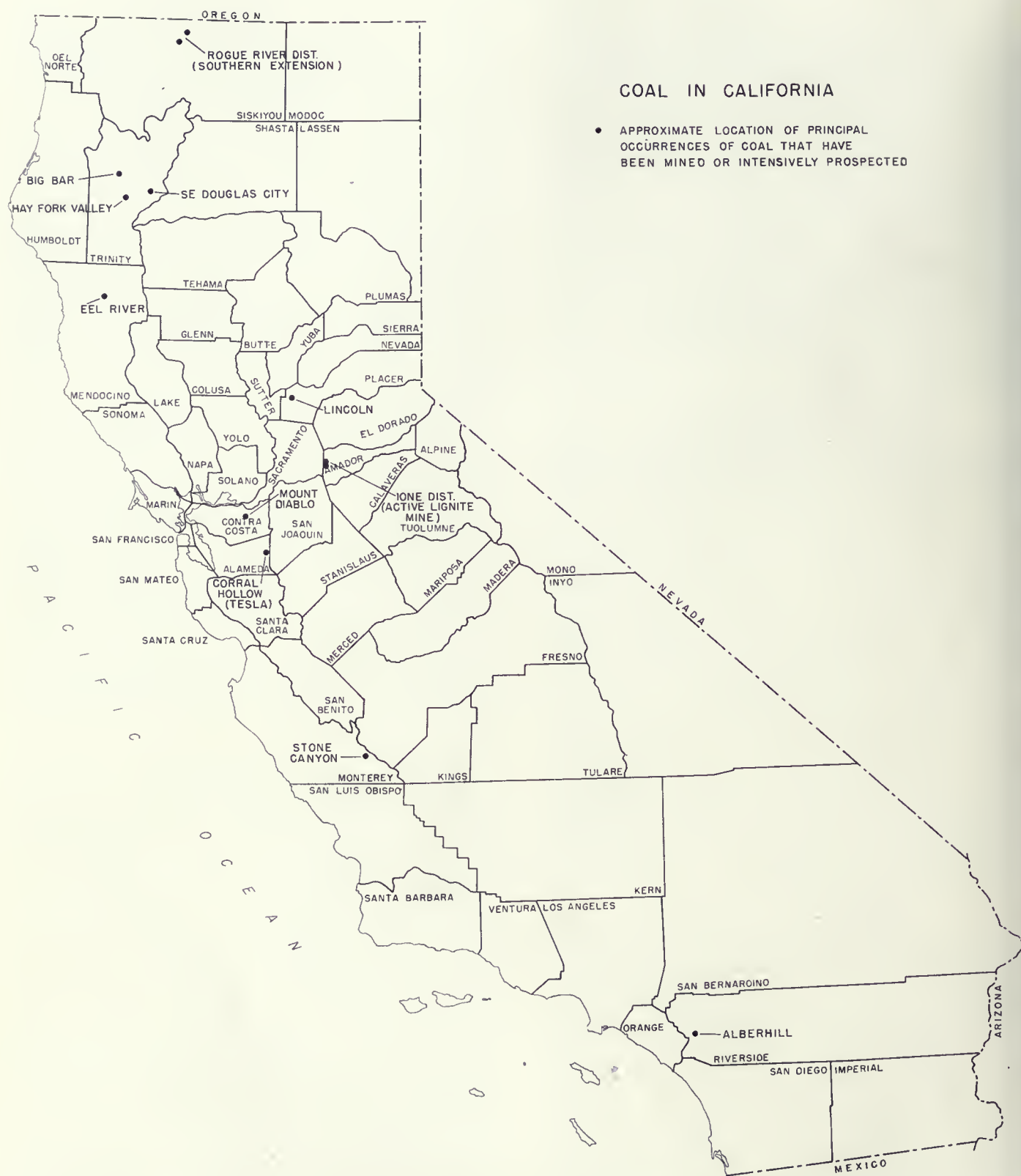


FIGURE 1. Map showing location of principal occurrences of coal in California that have been mined or intensively prospected.





FIGURE 2. View of Nortonville, Mt. Diablo district, in the late 1870s. The extensive mine dumps of the Black Diamond mine are prominent in the left foreground. (Photo courtesy W. F. Jones, San Francisco).

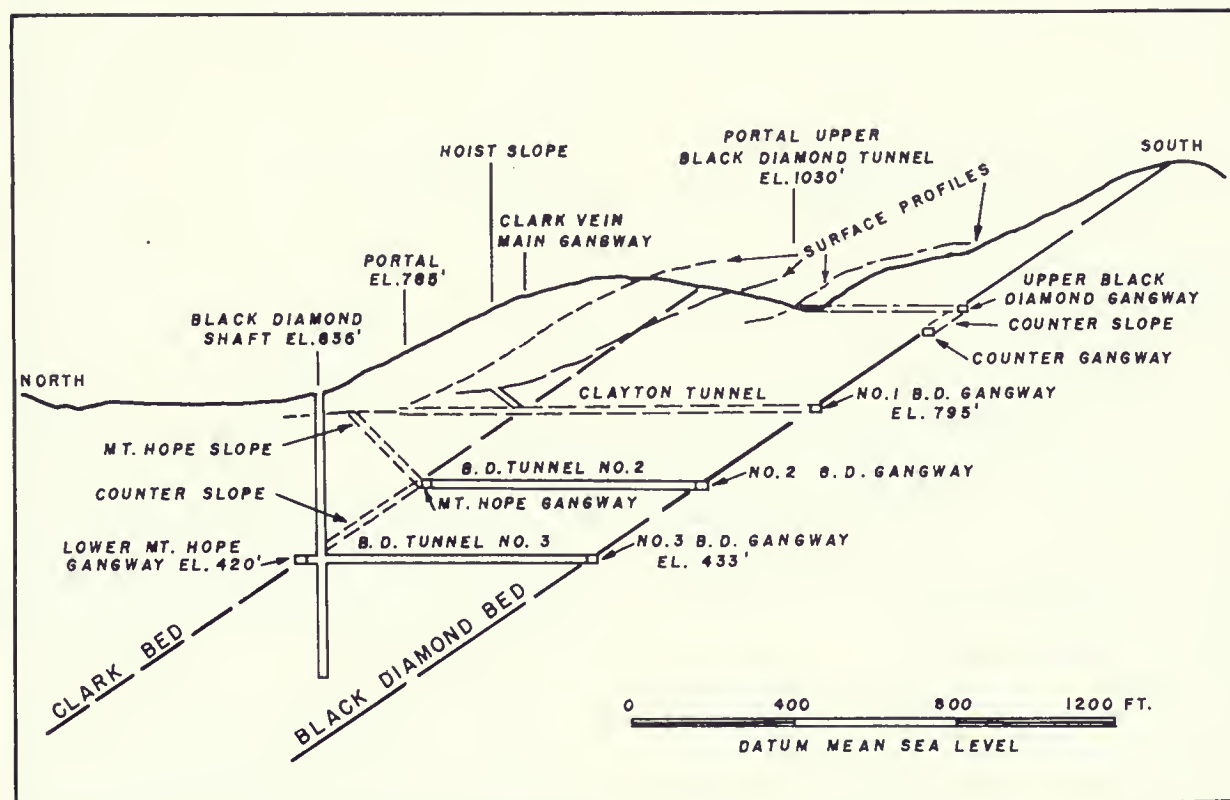


FIGURE 3. North-south cross section through the Black Diamond shaft of the Black Diamond coal mine, Contra Costa County. Workings shown by broken lines are projected to section. (Courtesy of Southport Land and Commercial Company, published in *California Jour. Mines and Geology*, vol. 47, no. 4).





FIGURE 4. Site of Tesla coal mines in Corral Hollow, Alameda County. In 1904 these mines were the principal source of coal in the state. Coal beds lie in middle Eocene Tesla formation.

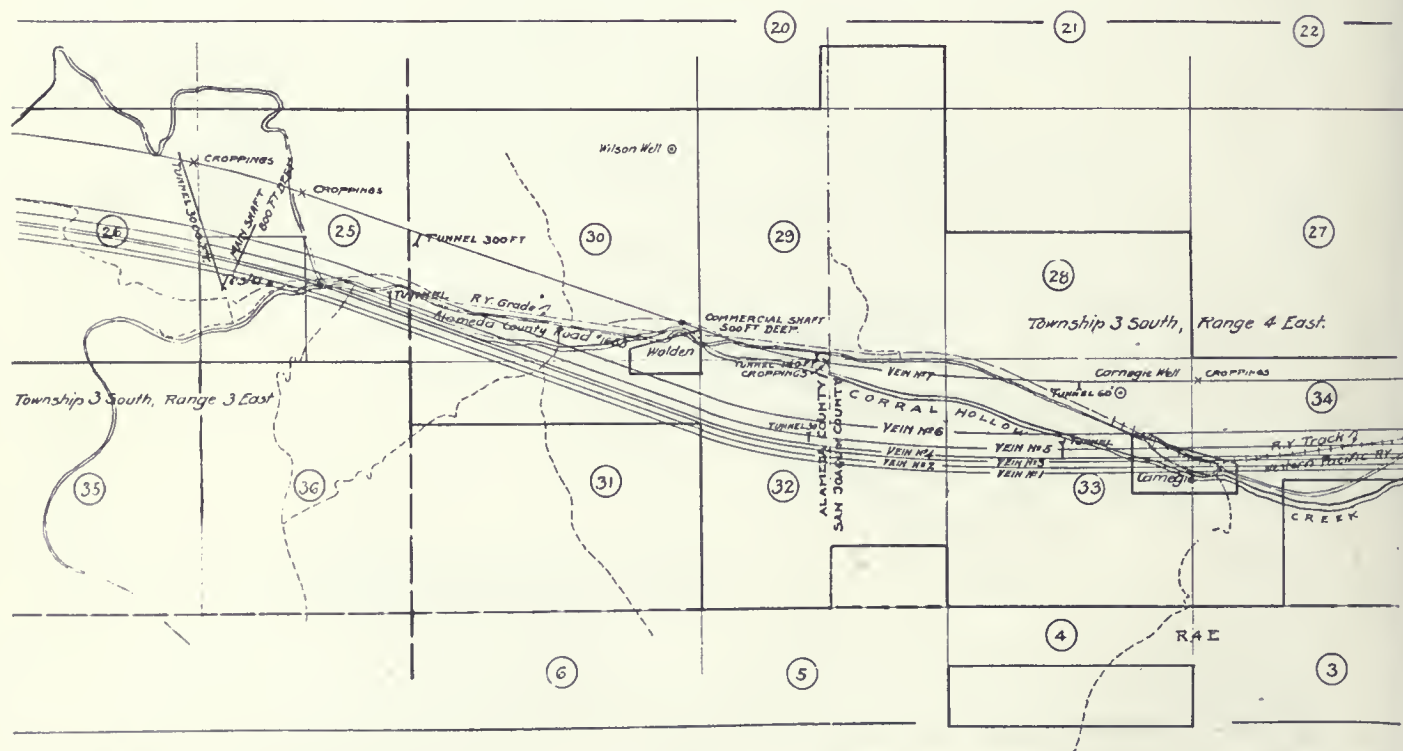


FIGURE 5. Map of Corral Hollow district, Alameda County, showing coal outcrops and probable extension of coal beds. (Map by Beckman and Linden Engineering Corporation October 1919, published in *California Dir. Mines and Mining Bull.* 99).



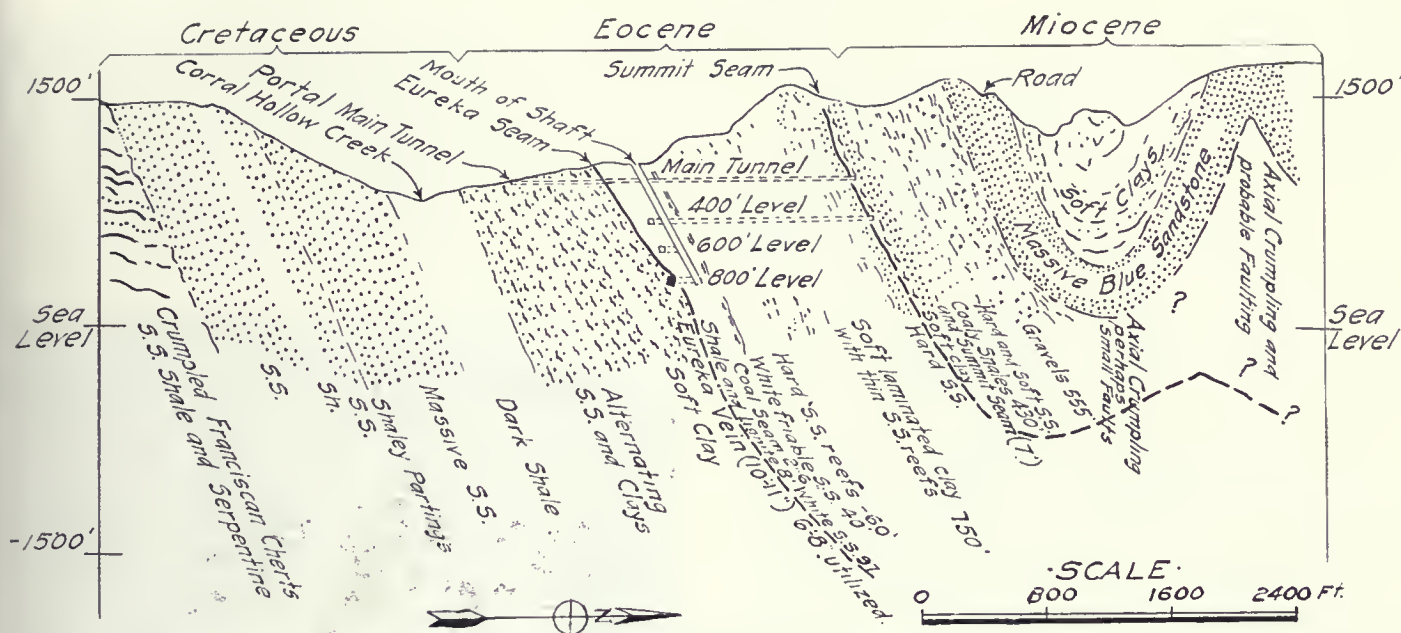


FIGURE 6. Generalized north-south geologic section through Corral Hollow district. (Map by Beckmon and Linden Engineering Corporation, October 1919, published in California Div. Mines and Mining Bull. 99).

which made mining dangerous and expensive. At some places in the district smaller coal seams, that occur between the Clark and Black Diamond seams, were developed.

The coal was mined by the breast-and-pillar method and workings reached a depth of 750 feet below the surface. The coal was sufficiently clean to be shipped without processing. Much of the accessible coal was worked out in the early days, and the tonnages that remain are not known. The white sand associated with the coal has been mined in more recent years for manufacture of glass, and for foundry and refractory purposes (Wright, 1948, p. 42).

In general, the surface coal is deeply weathered, but the quality of the coal improves downward to 200 feet below the surface. The coal has been classed by the U. S. Bureau of Mines as sub-bituminous.

**Corral Hollow District, Alameda County.** Deposits of coal at Corral Hollow near Tesla in Alameda County were discovered about 1857. For a few years, beginning in 1897, these deposits were intensively developed and for 5 years production averaged more than 70,000 tons per year. In 1904, the Tesla mines were the principal sources of coal in the state, but the same factors that caused the economic collapse of the Mt. Diablo coal fields also forced the Tesla mines to shut down a few years later.

The coal beds in Corral Hollow, like those at Mt. Diablo, are in middle Eocene sediments here called the Tesla formation (Huey, 1948). A surface map of the Tesla area (fig. 5) shows the lateral extent of the coal veins. A generalized geologic cross section through the main Tesla shaft (fig. 6) shows that the coal seams lie on the south limb of a steeply dipping syncline and are inclined about 70 degrees. Several coal bearing zones occur at this locality, but only the Eureka and Summit seams were large enough to be worked. The Eureka

seam is about 10 to 12 feet thick with a solid sandstone roof. Most of the mining was done on this bed and the coal was followed to a depth of 800 feet. The Summit seam averages 7 feet of clean coal but the overlying beds are shaly and require expensive timbering (Smith, 1902, p. 501-504).

The coal is classed as sub-bituminous by the U. S. Bureau of Mines (Andrews, 1947). Coal from this field was of uniform quality, burned freely, and had an ash content of about 8 to 9 percent. The coal seams were reached by both tunnel and shaft, and the breast-and-pillar system was used to mine the ore. Coal from the Summit seam was clean enough to go directly to the bunkers, but coal from the Eureka seam required screening and washing. In developing the coal mine, extensive deposits of commercial clay and high-grade quartz sand were discovered. The clay deposits continued to be worked several years after the coal mining ceased. Currently (1956) a quartz-clay mixture, known as "Livermore ganister", is being mined at the site of the old Tesla coal workings and is used as a foundry material (Wright, 1948, pp. 48-50).

**Stone Canyon District, Monterey County.\*** A coal deposit at Stone Canyon, Monterey County, which was discovered in 1870 and opened in 1907, contains some of the highest-rank coal in the state. In 1909, the mine was vigorously worked and yielded nearly 46,000 tons of coal, but as the San Francisco market was flooded with low-priced Australian coal, the mine did not show a profit. Late in 1909, heavy floods and a cloudburst damaged the property, and in October the company passed into the hands of a receiver. In 1921, the mine was opened by the Stone Canyon Coal Company which was financed by officials of the Inland Steel Company of

\* Many of the data presented herein were kindly provided in 1955 by T. O. Evans, Chief Mining Engineer, Santa Fe Railway Company, who was mining engineer at the Stone Canyon mine in 1921.



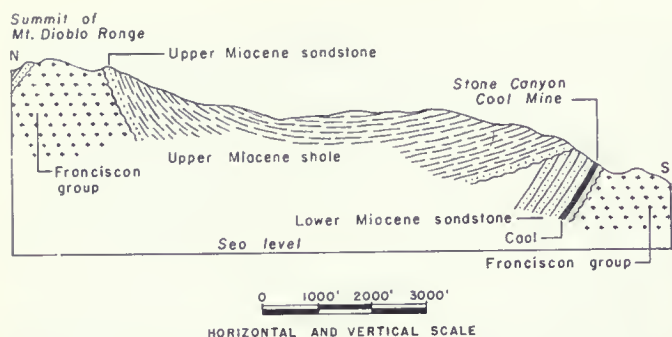


FIGURE 7. North-south geologic cross section through Stone Canyon coal district. (Modified after Arnold, 1905).

Chicago. The eastern end of the property was developed and about 50,000 tons of coal were produced during the  $1\frac{1}{2}$  years the mine operated. Practically all of this output was used for domestic purposes, but a lagging market forced the mine to close in 1922. The mine was reopened in 1931 by the Atlas Smelting Mining and Refining Company of San Francisco, which produced an estimated 10,000 tons of coal during the year it operated.

The coal has been mined from a single bed about 12 feet thick, which strikes northwesterly and generally dips northeasterly about 75 degrees, but occasionally dips as low as 12 degrees. Diamond drill data indicate that the total length of the coal bed along the strike does not exceed 1 mile (T. O. Evans, personal communication). The local structure, as shown by the accompanying cross section, is essentially a syncline consisting of upper Miocene Santa Margarita sandstone and shale which rest unconformably on the lower Miocene Vaqueros formation. The Vaqueros formation, which contains coal near its base, rests unconformably upon the Upper Jurassic (?) Franciscan complex. Locally, the Vaqueros-Franciscan contact is marked by a zone of faulting.

Early mining consisted of an inclined shaft 350 feet in depth sunk nearly on the coal bed, and a drift located 1500 feet southeast of the shaft and extending 3000 feet in a southeasterly direction along the coal seam. In 1921, the coal was mined by sinking an inclined shaft from the 300-foot level down the dip of the coal seam for 758 feet. Eleven rooms 24 feet wide were opened on each side of the shaft. When the mine was reopened in 1931, the No. 1 shaft was extended from the 300-foot level to the 600-foot level. About 10 rooms were opened up on the 600-foot level and extended for about 1000 feet.

The coal in Stone Canyon is a high-volatile bituminous coal, which is hard and does not slack readily on exposure. Many unsuccessful attempts were made to produce a satisfactory coke from the coal. A very fragile coke breeze (fragments finer than  $\frac{1}{2}$  inch) was made by the operators of the mine in 1921, but this material could not be marketed. A U. S. Geological Survey report (Arnold, 1906) states that Stone Canyon coal is non-coking. This was also found to be the case by Mr. T. O. Evans, the mining engineer in charge of the mining operations in 1921 (personal communication).

*Ione District, Amador County.* Lignite beds in the Ione region, about 36 miles southeast of Sacramento,

were mined for local use in the early 1860s. Commercial development of the fields started in 1888, and during the period 1888-1903 moderate amounts of coal were marketed in the Sacramento and San Joaquin Valley area. Production from this region from 1903 to 1947 was sporadic. In 1948, coal mining was resumed, but this time not for fuel purposes. The Ione lignite was found to contain a high percentage of wax suitable for industrial purposes and now Ione deposits make the United States self-sufficient in montan wax.



FIGURE 8. Lignite strip mine, one mile west of Ione. Source of lignite for American Lignite Products Company montan wax extraction plant. Coal bed is about 12 feet thick. (Photo by Mort D. Turner, 1950).

The American Lignite Products Company, Incorporated, set up a plant at Ione in 1948. This is the only operating montan wax plant in this country. The process\* of extracting montan wax begins by crushing the lignite to approximately  $1\frac{1}{2}$ -inch particles and then pulverizing them in a hammer mill (see flow sheet, fig. 9). The finely ground lignite is fed to an extractor where petroleum solvents remove waxes, wax esters, resins, and asphaltic substances. The slurry from the extractor is separated into filtrate extract and spent lignite by filters. The solvent is recovered from the extract in steam-heated stills and the liquid wax is pumped and transferred to a wax flaker. The flaked wax is bagged for shipment. Approximately 200 to 280 pounds of crude montan wax is obtained from 1 ton of lignite of 25 percent moisture content. The finished product is a hard, brown material which is marketed under the brand name Alpeo, Type 16.

The Ione formation (middle Eocene), in which the lignite beds occur, is a series of clay, shale, and sandstone beds exposed in isolated patches along the eastern edge of the Central Valley of California, from Cherokee in Butte County south to Daulton in Madera County. At some localities, notably near the town of Ione in Amador County, the formation contains large amounts of brown lignite. This lignite occurs in lens-shaped bodies ranging in diameter from 500 to 3,000 feet. These bodies are reported to be as much as 24 feet thick, nearly flat-lying, and rarely deeper than 125 feet. Figure 10 is a surface map showing the coal basins in Amador County. At the

\* The following description has been approved for publication by Mr. F. J. DeAngelis of the American Lignite Products Company, August 1956.



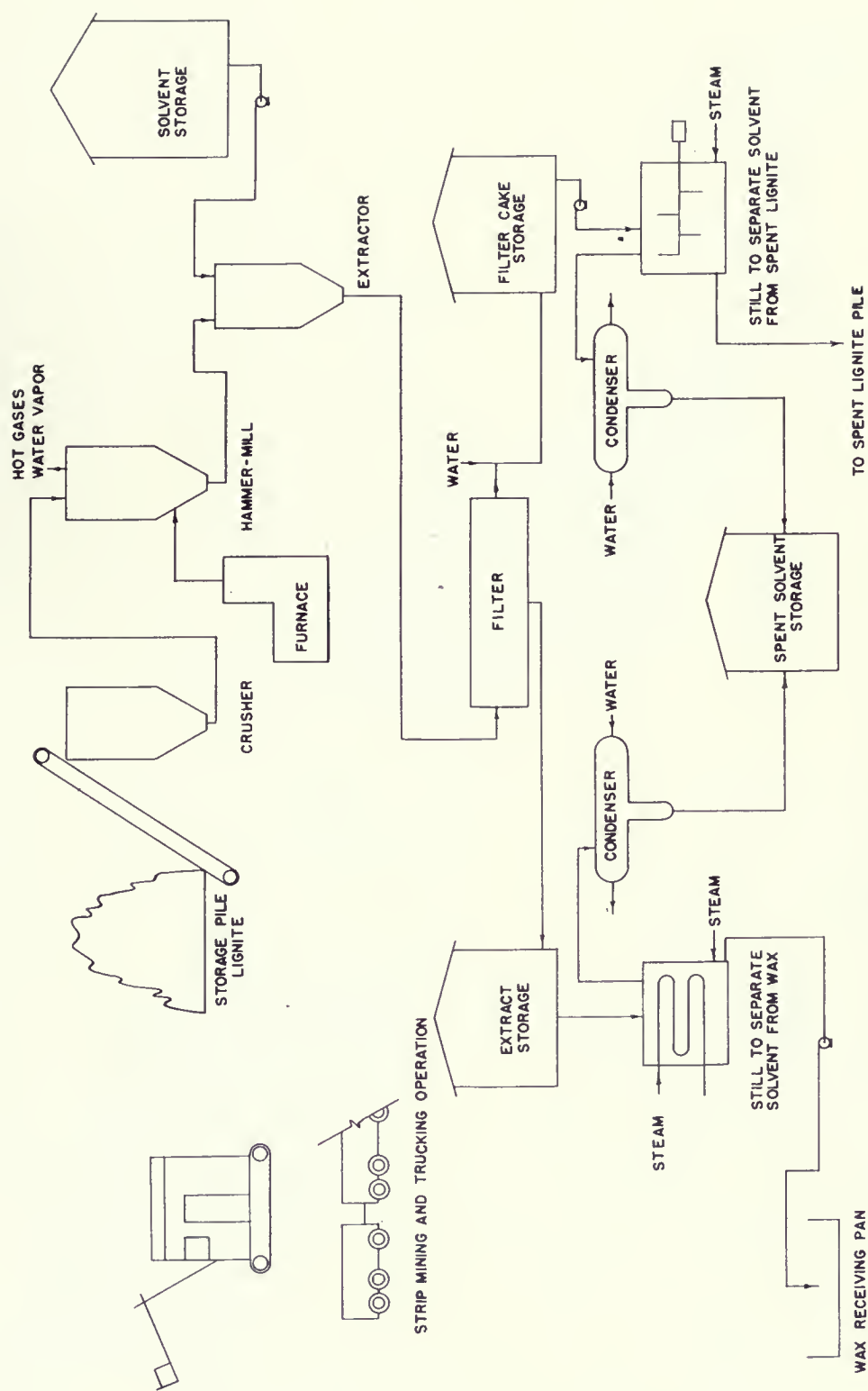


FIGURE 9. Process diagram: extraction of montan wax from lignite, American Lignite Products Co., Lone, California. (*U. S. Bureau of Mines, Inf. Circ. 7692*).



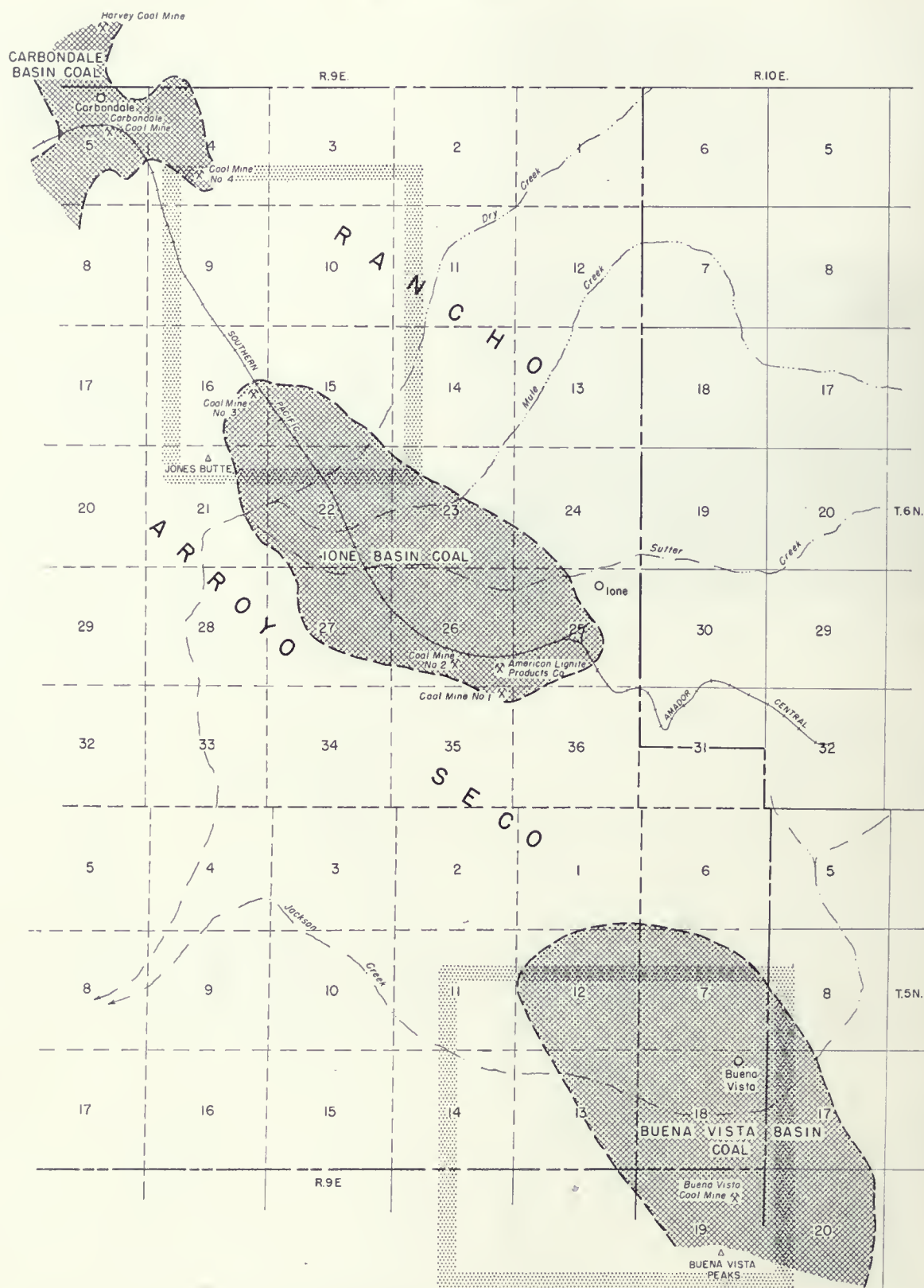


FIGURE 10. The coal basins of Amador County. Boundaries are fairly definite for the east and west sides of the Buena Vista basin, the south side of the Ione basin and the portion shown of the Carbondale basin. Other boundaries are approximately located. (Modified by Mort D. Turner from unpublished maps by Mocine, 1923 and McCready, 1927). Areas within stippled borders are described in California Journal of Mines and Geology, July 1949, and in California Division of Mines Special Report 19.



American Lignite Products Company mine near Ione, the lignite is strip-mined by means of a dragline. Here the overburden ranges from 18 to 44 feet in thickness. In 1956, this was the only continuing coal operation in California. Another operation, that of the Humacid Company, near Buena Vista, was active from 1951 to 1952. This was entirely an underground operation where a lignite bed 75 feet below the surface was developed. Drill holes revealed two deeper beds, one at about 85 feet and the other at 100 feet. Plans for building a montan wax extraction plant for the Humacid coal mine did not materialize, and the mine shut down.

**Alberhill Area and Santa Ana Mountains, Riverside and Orange Counties.** Many coal seams have been encountered in clay quarries of the Alberhill and Santa Ana Mountain areas of southern California. The seams occur in the Silverado formation (Paleocene) and are classed as lignite.

At Alberhill, coal was mined from 1885 to about 1900. The coal occurs in a single layer with a maximum thickness of 10 feet and an average thickness of about 4 feet. It rests between a clay floor and a sandstone roof about 85 feet below the surface and dips about 3 to 10 degrees. Most of the coal was mined from the property now held by the Alberhill Coal and Clay Company. Coal is still removed in the present clay mining operations, but is considered to be of little commercial importance.

**Eel River District, Mendocino County.** Deposits of coal have long been known in the Eel River district, Mendocino County, 175 miles north of San Francisco. A small amount of coal from this district was marketed in the period 1923-26, and about 40 tons were mined and shipped in 1948.

The deposits are four miles east of Dos Rios on property belonging to the Flood Estate. The coal lies within isolated patches of the middle Miocene Temblor formation which are down-faulted into the underlying Franciscan (Jurassic ?) sandstone. Where Salt Creek joins the Middle Fork of the Eel River, a prominent bed of coal 14 to 15 feet thick dips about 20 degrees NE and crosses the channel of the latter. Figure 11 is a map showing the discontinuous, northwesterly trending coal outcrops in this area. The region contains numerous landslides and many faults which make it hazardous to predict the lateral continuity of the coal below the surface. Analyses by the U. S. Bureau of Mines (Reynolds, 1946) of two samples of coal from this district indicated a sub-bituminous rank and a non-coking grade.

**Trinity County.** Lignite has been mined at Big Bar and at the Reese Brothers mine southeast of Douglas City, and at a few other prospects in Trinity County (Averill, 1941). The mining operations have been small and the coal has only been used locally for domestic purposes.

The coal in Trinity County is of Cretaceous and Eocene age. Lower Cretaceous coal at Big Bar has been mined intermittently since 1929, but an 80-mile truck haul to railroads makes transportation a problem. The coal beds are interbedded in shale and sandstone, which dip about 30 to 40 degrees, but only one bed, 3 to 5 feet thick, was found to contain coal clean enough to be mined. The lateral extent of these beds has not been determined. Lignite beds in the Eocene Weaverville for-

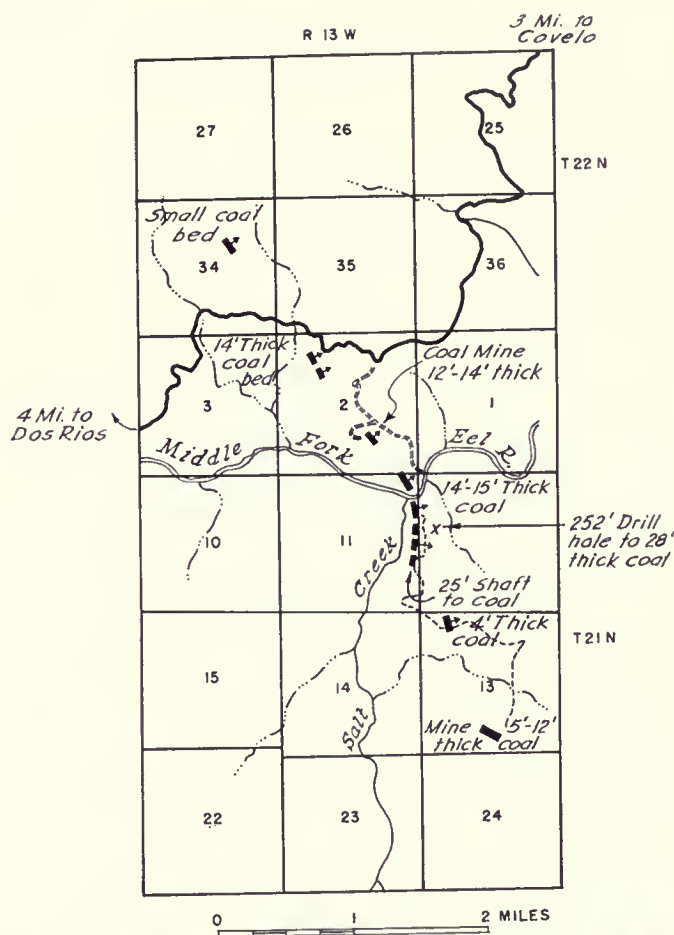


FIGURE 11. Map of Dos Rios coal area, Eel River District, Mendocino County, showing outcrops of coal.

mation at the Reese Bros. mine are 8 feet thick, dip about 20 degrees, and are interbedded with volcanic ash. A small production was reported in 1946.

#### UTILIZATION OF CALIFORNIA COAL

As coal found in California is generally of lignite or sub-bituminous rank, it has a low heating value, and generally makes poor fuel compared with coal mined in the Rocky Mountains and the eastern United States. California coal does not yield coke that is suitable for use in steel smelting. This is attributable to the high ash and sulfur content of the coal and to the weakness of the resulting coke. Coking coal for California's steel smelters is brought into the state, mostly from Utah and Oklahoma. California's only coking plant is located at the Kaiser Steel Company, Fontana, San Bernardino County. Table 2 summarizes the production data for this plant. Additional coke for California's industrial plants is brought in from other states. The source and distribution of this coke produced in other states is summarized in table 3. For additional information see "coke" under "iron and the iron industries" in this volume.

Lignite from Ione, California, has been found to yield a higher percentage of montan wax than any other lignite in the United States. Montan wax is hard and brittle and has a high melting point. These properties make it an important ingredient in certain shoe polishes, floor



Table 1. Analyses of California coals.\*

Mine	Rank	Moisture	Volatile matter	Fixed carbon	Ash	Sulfur	B t u
Mt. Diablo, Contra Costa Co.....	Sub-bituminous.....	15.0	38.4	34.5	12.1	5.6	9,240
Corral Hollow, Alameda Co.....	Sub-bituminous.....	18.0	39.2	26.4	16.4	3.1	8,105
Stone Canyon, Monterey Co.....	Bituminous.....	6.9	46.7	40.1	6.2	4.2	12,447
Ione, Amador Co.....	Lignite.....	22.4	42.4	20.4	14.8	2.9	9,322
Alberhill, Riverside Co.....	Lignite.....	19.0	46.5	21.9	12.6	--	--
Santa Ana Mts., Orange Co.....	Lignite.....	7.9	29.9	49.5	12.7	--	--
Eel River, Mendocino Co.....	Sub-bituminous.....	12.8	34.4	37.3	15.8	1.0	10,890
Fireflex (Trafton), San Benito Co.....	Sub-bituminous.....	15.9	33.7	39.6	10.8	4.4	9,691
Reese Bros., Trinity Co.....	Lignite.....	13.3	38.6	30.5	17.6	1.1	8,120

\* From various published sources.

waxes, electrical insulating compositions, impregnations and waterproofing, leather dressings, inks, carbon papers, protective coatings, greases, phonograph records, rubber, investment castings, and many other allied fields. Before World War II, montan wax was imported from Germany and Czechoslovakia, but since 1948 the montan wax plant at Ione has supplied most of United States

Table 2. California coking-plant data.

(From U. S. Bureau Mines Mineral Market Rept. M. M. S. No. 2520, Coke and Coal Chemicals in 1955)

<b>Oven Coke</b>	
Number of plants.....	1
Number of ovens (slot-type).....	225
Coke capacity of ovens (annual net tons).....	1,055,000
Coal carbonized (net tons).....	1,356,513
Yield of coke from coal.....	60.06%
Coke produced (net tons).....	814,687
<b>Coke breeze</b>	
Yield per ton of coal.....	4.95%
Produced (net tons).....	67,142
Sold (net tons).....	16,170
Used by producer (net tons).....	50,972
<b>Origin of coal shipped to California oven-coke plants (net tons):</b>	
Arkansas.....	9,174
Colorado.....	2,673
New Mexico.....	12,366
Oklahoma.....	223,591
Utah.....	1,121,743
Total.....	1,369,547
<b>Volatile content of coal shipped to California oven-coke plants:</b>	
High volatile <sup>1</sup> (net tons).....	1,136,782
High volatile <sup>1</sup> (percent of total).....	83.0
Low volatile <sup>2</sup> (net tons).....	232,765
Low volatile <sup>2</sup> (percent of total).....	17.0
<b>Production and disposal of coke-oven gas, in thousand cubic feet:</b>	
Total produced.....	15,570,471
Gas per ton of coal coked.....	11.48
Used in heating ovens.....	1,388,538
Used by producer in steel or allied plants.....	12,177,607
Sold for industrial purposes.....	1,581,045
Wasted.....	423,281
<b>Production of coke-oven by-products:</b>	
Ammonium sulfate (pounds).....	32,378,846
Ammonium sulfate (pounds per ton of coal coked).....	23.87
Tar (gallons).....	12,391,563
Tar (gallons per ton of coal coked).....	9.13
Crude light oil (gallons).....	4,530,667
Crude light oil (gallons per ton of coal coked).....	3.34
Benzene, in gallons (not motor grade).....	2,490,376
Benzene (percentage yield from crude light oil refined).....	55.2
Toluene (gallons).....	722,583
Toluene (percentage yield from crude light oil refined).....	16.0
Xylene (gallons).....	169,963
Xylene (percentage yield from crude light oil refined).....	3.8
Solvent naphtha (gallons).....	123,869
Solvent naphtha (percentage yield from crude light oil refined).....	2.7

<sup>1</sup> High volatile coal contains over 31 percent dry volatile matter.<sup>2</sup> Low volatile coal contains 14 percent to 22 percent dry volatile matter.

needs. General specifications of Alpeco wax, Type 16, manufactured at Ione, are shown in table 4. The residue from the wax-recovery operation at Ione is used in several ways: (1) as a drilling mud additive to control viscosity, (2) in the tanning industry, (3) as a pigment, and (4) as a filler in fertilizers. The spent residue is claimed to have fertilizing properties, act as mulch, improve soil porosity, restore organic matter, and contribute humic acid to the soil.

Investigations are currently being made by government agencies in the recovery of uranium in the ash of various coals, including lignites. During the summer of 1952, a reconnaissance was conducted in California by the U. S. Geological Survey in search of new deposits of uranium-bearing carbonaceous rocks (Moore and Stephens, 1954). The principal localities in California where uranium occurs in coal are listed as the Newhall prospect, Los Angeles County (0.020 percent uranium); Fireflex mine, San Benito County (0.005 percent uranium); American Lignite mine, Amador County (0.004 percent uranium); and Tesla prospect, Alameda County (0.003 percent uranium).

In 1951, an investigation of the synthetic liquid fuel potential of the state was made for the U. S. Army Corps of Engineers (U. S. Bureau of Mines, 1951). Consideration was given to oil-impregnated strippable deposits, coal, and natural gas as raw materials for synthetic liquid fuel. These investigations concluded that, although coal is widely distributed in California, the deposits are of small individual occurrence and not of sufficient size to meet the minimum requirements set up by the survey. The reserve requirements specified: (1) recoverable tonnage within an area of three miles radius be not less than 30,000,000 tons for underground mining or 5,000,000 tons for strip mining; (2) that the minimum thickness for underground mining be 24 inches for bituminous coal, 28 inches for sub-bituminous coal, and 48 inches for lignite, and that the minimum thickness for strip mining be 12 inches; and (3) that the maximum depth of coal for underground mining be not more than 1,500 feet below drainage level.

#### MARKETING DATA

Several properties of coal are important to its market value. The more important are as follows:

Fuel ratio (ratio of fixed carbon to volatile matter; this is high in anthracite and low in lignite).

Heating value (expressed in Btu).

Ash content (owing to silt, clay, silica, etc.; the less present, the better the quality of coal).



Table 3. Source and distribution of oven and beehive coke and breeze consumed in California in 1955.  
(From U. S. Bureau Mines Mineral Market Rept. M. M. S. 2540, Distribution of Oven and Beehive Coke in 1955)

Source	Coke (net tons)							Total breeze (net tons)
	To blast furnace plants	To foundries	To producer gas plants	To water and gas plants	To other industrial plants	For residential heating	Total coke	
Alabama.....	--	20,769	--	--	11,869	--	32,638	42
California.....	805,566	--	--	--	2,763	--	808,329	54,909
Colorado.....	--	--	--	--	1,666	--	1,666	43
Illinois and Missouri.....	--	22,543	--	--	6,897	--	29,440	--
Indiana and Kentucky.....	--	7,604	--	--	2,619	--	10,223	--
Michigan and Wisconsin.....	--	7,594	--	--	10,782	--	18,376	--
Minnesota.....	--	7,000	--	--	2,745	--	9,745	--
Ohio.....	--	12,091	--	--	6,570	--	18,661	77
Tennessee and Texas.....	--	190	--	--	--	--	190	--
Utah.....	--	112-120	--	--	20,721	--	20,721	558
West Virginia.....	--	225	--	--	--	--	225	--
Total.....	805,566	78,016	none	none	66,632	none	950,214	55,629

Table 4. General specifications, Alpeco wax, Type 16.  
(American Lignite Products Co., Ione, California)

Melting point, ASTM, D-127-49.....	187° F. + 3° F.
Hardness, at 77° F., Shore Durometer.....	100
Penetration, 100g/5 Sec/77° F., ASTM, D-5-52.....	0-1
Acid value, mg. KOH/g.....	48-53
Saponification value, mg. KOH/g.....	112-120
Ash.....	0.2 Max.
*Benzol solubility, hot.....	Complete
Benzol solubility at 32-40° F. (resinous matter).....	20% Max.
*Methyl-Ethyl-Ketone, hot, solubility.....	100%
Color streak.....	Brownish
Fracture.....	Conchoidal
Specific gravity.....	1.02-1.03
Ultimate Analysis (%)	
Ash.....	0.2
H.....	12.2
C.....	79.4
N.....	0.0
S.....	0.3
O-(by diff.).....	7.9

\* One gram of wax per 100 cc. solvent.

Storing and weathering qualities.  
Moisture content.

Coking qualities (a good coke should contain not more than: 1.5% sulfur, 0.04% phosphorus, 3% moisture, 10% ash, 2% volatile matter; should contain about 85-90% fixed carbon; consist of large lumps, usually 60-70% larger than 2 inches; and be hard and strong to resist breakage.

If the coal is to be used for manufacture of montan wax, then the wax content is of prime importance and the other factors listed above are of no consequence. A wax content of about 10 percent is estimated to be necessary in order for coal to be economically suitable for montan wax manufacture.

The montan wax (Alpeco, Type 16), which is marketed by the American Lignite Products Company, Amador County, sells for 26.5 cents per pound f.o.b. Ione. A semi-refined wax, which has a lighter color than Type 16, was to be available by late 1956 and was to be sold for about 45 cents per pound. Manufacture of a fully refined wax to be sold for 60 to 65 cents per pound (f.o.b.) was also planned for 1957.

Intermittently small amounts of coal are produced and sold locally in California for domestic heating purposes.

Manufacture of coal briquets has been unsuccessfully attempted in the past, the latest attempt being in the Ione area during 1946-1948 while fuel oil was scarce in California (F. J. De Angelis, American Lignite Products Company, personal communication). The operation ceased when fuel oil again became available.

Considering the area and population of California, relatively small tonnages of coal are consumed in this state. The largest single use for coal in California is in the production of coke for the Kaiser Steel Company blast furnaces; for this purpose, 1.3 million tons of coal were imported from other states during 1955. A few hundred thousand tons of coal are used annually in small amounts for various industrial applications, blacksmithing, and domestic heating. Industrial applications commonly make use of coal as a source of carbon required in certain processes. For example, the Selby smelters use annually approximately 15,000-20,000 tons of coal in the reduction of lead-zinc ores. Foundries use finely ground anthracite or bituminous coal, commonly called "sea coal," to apply on foundry facings. A few brick plants use bituminous coal to fire their kilns; one brick plant in the S. F. Bay area uses 180 tons of Utah coal per month. The current delivered price (1956) for car-load lots of lump coal in California ranges from about \$11.00 to \$20.00 per ton, depending upon the rank and size of the coal. As long as oil and natural gas continue to be the primary sources of energy, it is unlikely that California will require much more coal than it uses at present.

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## COBALT

BY CHARLES W. CHESTERMAN

Minor occurrences of cobalt-bearing minerals have been reported from numerous localities in California (Murdoch and Webb, 1948, pp. 114, 139-140), but there has been very little commercial production of cobalt in the state. Most of the discoveries of cobalt minerals have been made in well-known zones of mineralization, such as the Sierran Foothill copper belt (Logan, 1925, p. 142), and the zinc-lead districts of southern California (Gay and Hoffman, 1954, p. 493).

**Mineralogy.** Nearly all cobalt ore is associated with one or more of the following metals: copper, nickel, iron, lead, zinc, arsenic, manganese, silver, and gold. The important ores of cobalt are smaltite, cobaltite, linnaeite, erythrite and asbolite. Smaltite ( $\text{CoAs}_2$ ) is the principal cobalt arsenide and is the chief cobalt-bearing mineral at many deposits in Germany, Canada and French Morocco. It is gray in color, has a metallic luster, a specific gravity of 6.5, cubic structure, and contains 28.2 percent cobalt. Cobaltite ( $\text{CoFeAsS}$ ) is associated with cobalt arsenides in the cobalt districts of Burma, Ontario and Australia. It is a grayish mineral, has a metallic luster, a specific gravity of 6.3, and contains, when pure, 35.5 percent cobalt.

Linnaeite ( $\text{Co}_3\text{S}_4$ ) occurs in the cobalt ores of the Belgian Congo and in the lead-zinc deposits in the Mississippi Valley, United States. In color it is light gray to steel-gray, has a metallic luster which tarnishes easily to copper-red, a specific gravity of 4.5, and contains from 31 to 40 percent cobalt. The cobalt may be replaced in part by nickel. Erythrite ( $3\text{CoO} \cdot \text{As}_2\text{O}_5 \cdot 8\text{H}_2\text{O}$ ) generally occurs as an oxidation product of cobalt arsenides and sulfides. It ranges in color from pale pink to orange red, has a specific gravity of 3.0, perfect cleavage, and contains, when pure, 29.5 percent cobalt. Asbolite (an impure mixture of manganese and cobalt oxides) is the principal cobalt material of New Caledonia and has been found in small quantities at several places in California. It is dull black in color, has a specific gravity of about 1.1, hardness of 1 to 2, and a cobalt content in the range of 4 to 35 percent.

**General Geology.** The bulk of the world's output of cobalt comes from the Katanga region of the Belgian Congo, Northern Rhodesia, the Bou Azzer district of French Morocco, the Sudbury and Temiskaming districts of Canada, the Cornwall magnetite deposit of Pennsylvania, and the Blackbird district, Idaho. The cobalt minerals are mined from replacement deposits in pre-Cambrian dolomitic limestone; from veins formed at the contacts between serpentine and dolomite; from lateritic soils developed on serpentinized peridotites; from deposits formed in pre-Cambrian sedimentary rocks and diabases; and from deposits formed by the intrusion of diabase sills into Triassic shales and a Cambrian limestone. The reserves of cobalt ore in the principal producing districts are large, and several of the larger districts contain reserves far in excess of 100 million tons, ranging in grade from 0.05 to 5.0 percent cobalt.

In 1953, the domestic sources of commercial cobalt in the United States were as follows: (1) the Cornwall

mine of the Bethlehem Steel Company, Cornwall, Pennsylvania, (2) the Blackbird mine of the Calera Mining Company, Blackbird district, Idaho, (3) Sullivan Mining Company, Kellogg, Idaho, which recovers cobalt from zinc ores mined from their deposits in the Coeur d'Alene district, and (4) the St. Louis Smelting and Refining Division of the National Lead Company, which treats ores from deposits in the Fredericktown area in the southeastern Missouri lead district.

At the Cornwall mine, cobaltiferous magnetite occurs at the contact of a diabase sill with Triassic calcareous shale. The magnetite has been mined for many years for its iron content, but the cobalt was not recovered commercially until 1940. The cobalt ore at the Blackbird mine of the Calera Mining Company, Idaho, occurs as replacement bodies in shear zones in the primary mineral—cobaltite; also as the pink and green secondary cobalt minerals—erythrite and annabergite, respectively. The ore carries about 0.6 to 0.8 percent cobalt, about twice as much copper, and some gold and nickel. Although the presence of cobalt in the Blackbird district was known as early as 1895, it was not produced commercially until 1918. In 1951, the Calera Mining Company completed a concentrator and began shipments of concentrates to the company refinery at Garfield, Utah. In 1953, the first cobalt granules were produced at this smelter and averaged about 95.5 percent cobalt and 4 percent nickel. The reserves of cobalt at the Blackbird district are large, and in the latter part of 1949, more than 1,743,000 tons of ore containing 0.74 percent cobalt and 1.59 percent copper were blocked out (Davis, et al., 1952, p. VI-42). The Calera Mining Company was the chief domestic producer of cobalt in 1953 (Davis and Buck, 1953, p. 2).

The cobalt recovered in 1953 by the Sullivan Mining Company, Kellogg, Idaho, was obtained at its electrolytic zinc plant.

Cobalt has been produced intermittently since 1910 from the Fredericktown area in the southeastern Missouri lead district. Here sulfides of cobalt and nickel are associated with sulfides of iron, lead, and copper in Cambrian carbonate rocks. In 1953, the reserves of cobalt ore at the property of the St. Louis Smelting and Refining Division of the National Lead Company, the principal cobalt producer in the Fredericktown area, were reported to be in excess of 4,000,000 tons carrying 2.29 percent lead, 1.43 percent copper, 0.46 percent nickel, and 0.28 percent cobalt (Davis, Moore and Vhay, 1952, p. VI-44).

**Localities in California.** A few tons of cobalt ore were mined at the Mar John property in Calaveras County in 1924, but were not marketed. A sample of cobalt ore taken from mineralized zones in a roof pendant of pre-Cretaceous schist, marble, and lime silicate hornfels on Long Lake, Inyo County, was found to contain 0.88 percent cobalt, 0.69 percent copper, and 0.11 percent nickel. A four-inch quartz vein in a shallow adit assayed 0.53 percent cobalt (Davis, Moore and Vhay, 1952, p. VI-38).





FIGURE 1. Map showing cobalt occurrences in southern California. 1, Long Lake area, Inyo County; 2, Julian-Cuyamaca area, San Diego County.

At the Friday mine, Julian-Cuyamaca area, San Diego County, as much as 0.15 percent cobalt is present in the massive sulfides which consists principally of pyrrhotite with minor amounts of chalcopyrite, pentlandite, pyrite, and violarite. The massive sulfides form an irregular body replacing the Cuyamaca gabbro (Mesozoic), at the contact between the gabbro and a large inclusion of schist (see section on pyrites for discussion of the Friday ore body) (Creasy, 1946, pp. 24-27).

**Recovery.** Medium- to high-grade cobalt ores, ranging from 4 to 12 percent cobalt, are fed directly into the smelter. Low-grade ores, containing less than 4 percent cobalt, and those whose metallic components are in the oxidized state are concentrated. They are treated either by bulk flotation, or by washing, picking and jigging; the treatment depending upon the nature of the ore. The middlings are subjected to flotation. The recovery of cobalt from its ores is a complex metallurgical process involving stages, different pieces of equipment and reagents. In general, the concentrated ore is roasted to produce an alloy, matte, or speiss, depending upon the type of ore. This product is then refined by involved chemical or electro-chemical methods.

**Utilization.** Cobalt is a metal which combines readily with iron, nickel, aluminum and copper to form magnets

and high temperature alloys, and with other chemicals to produce cobalt salts and driers, both of which have innumerable uses in the manufacture of paints, varnishes and colored glasses.

The largest single use for cobalt is for cobalt-chromium-tungsten-molybdenum alloys which, in 1953, accounted for 21 percent of the total consumed. High temperature alloys that contain cobalt as one of the principal constituents have many uses, depending upon the composition of the alloy. Vitallium (Co = 64%, Cr = 27%, Ni = 2%, and Mo = 5%) is used for various parts of jet engines, turbosuperchargers, and gas turbines. Another alloy manufactured by the General Electric Company, referred to as HS-23 61 Nr-60 (Co = 66%, Cr = 28%, and W = 6%) is used for blades for jet engines and locomotive turbines.

Permanent magnets are used in many types of electrical meters, regulating devices, switching appliances, relays, and in the laboratory to separate magnetic from non-magnetic materials. They are composed of several metals in varying proportions, ranging from 5 to 50 percent cobalt, 6 to 12 percent aluminum, 14 to 45 percent nickel, 38 to 63 percent iron, 3 to 50 percent copper, and minor amounts of titanium, vanadium, manganese, molybdenum and chromium.



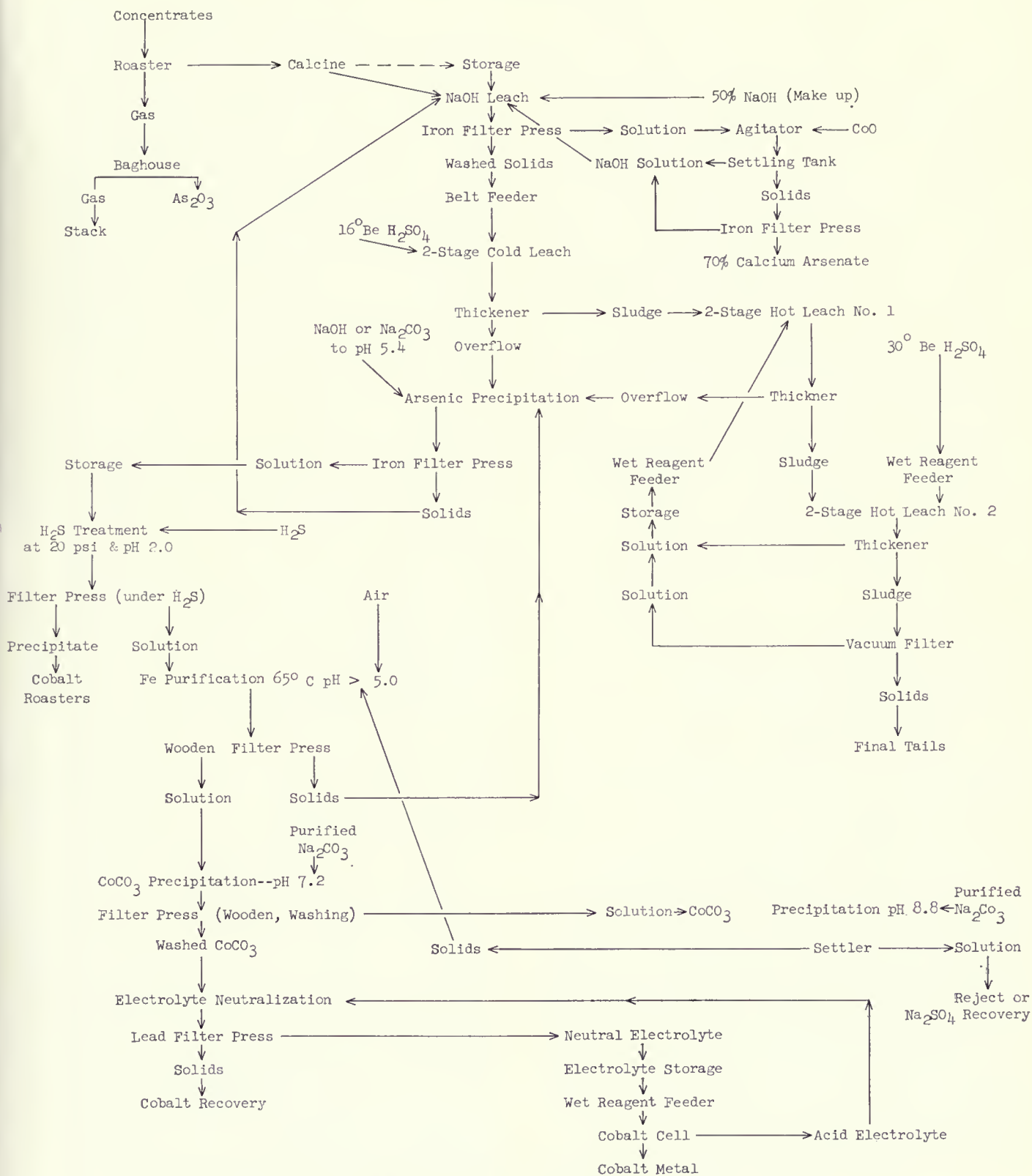


FIGURE 2. Flow sheet of cobalt production from concentrates from Blackbird mine, Forney, Idaho.  
(After Davis, Moore, and Vhay, 1952.)



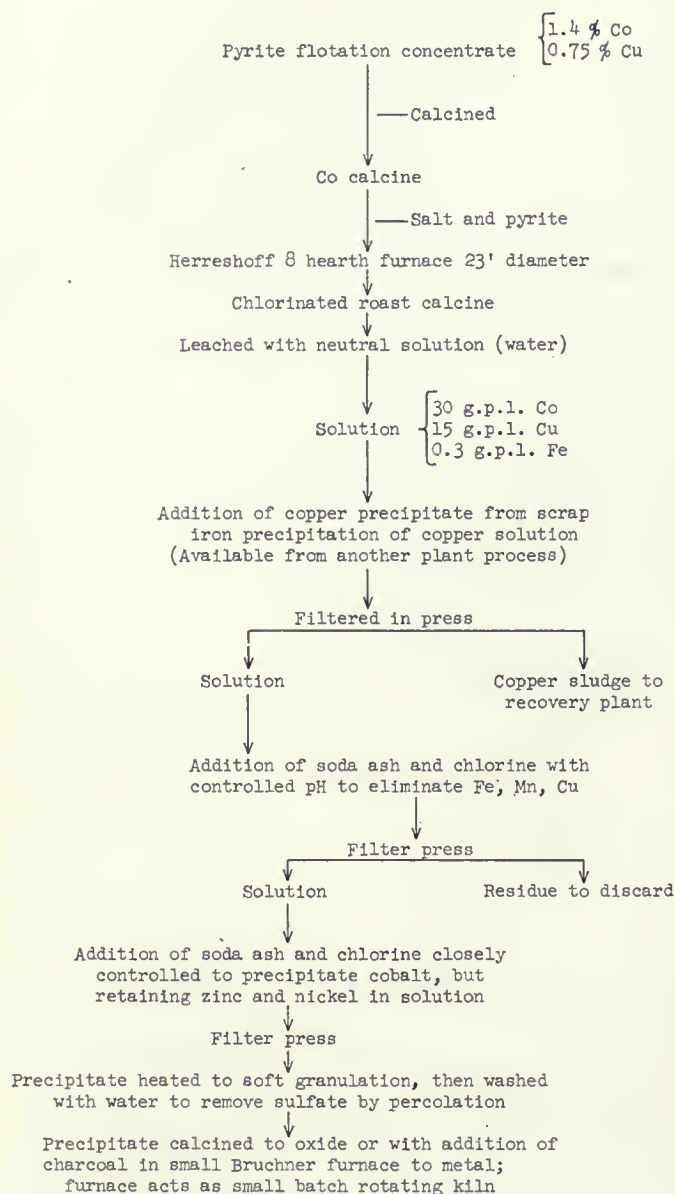


FIGURE 3. Flow sheet of cobalt production of Pyrites Co., Wilmington, Del. (After Young, 1948.)

The rest of the cobalt consumed in the United States (37 percent in 1953), is used principally in steel alloys, especially high-speed steels, and for the manufacture of various salts, driers and pigments. In the ceramic industry, cobalt is used in the manufacture of ground coats for porcelain enamelware. Cobalt oxide is used for this purpose as it produces the best bond at the steel-enamel interface. Considerable cobalt is also used in the manufacture of blue glass for medicine bottles. In addition, cobalt oxide is used to counteract the yellow stain imparted to ceramic bodies by iron in the clay.

Cobalt is used in the manufacture of fast-drying paints and enamels. Driers are essentially catalysts

added to drying oils to accelerate their oxidation and polymerization. Cobalt is also used as a catalyst in many organic chemical reactions, such as some hydrocarbon cracking processes (Davis, Moore and Vhay, 1952, pp. x-3 to x-18).

**Marketing.** The problems relating to the marketing and distribution of cobalt metal in the United States are few and simple, since there are just a few sources of the metal. For the past few years the price for metallic cobalt has shown very little fluctuation and deliveries generally are made on contract basis. In Canada, on the other hand, the Deloro Smelting and Refining Company purchases silver-cobalt ores and concentrates from mines in northern Ontario on an established schedule (Davis, Moore, and Vhay, 1952, p. IV-4-5). The cobalt-bearing concentrates shipped from Calera Mining Company's mine in the Blackbird district, Idaho, to their refinery at Garfield, Utah, contain at least 17 percent cobalt, 25 percent arsenic, 25 percent iron, and trace amounts of nickel, copper, gold, and silver.

Cobalt metal is marketed in the United States as rondelles, granules, powder, and fines. The cobalt granules are not sold to any particular specification as to screen size. All of the cobalt fines marketed in the United States are used as raw material for the manufacturing of salts and driers. The production of cobalt powder is small. Most consumers prefer to purchase the metal or oxide and manufacture their cobalt powder to meet their own specifications.

The price of metallic cobalt has ranged from \$1.00 to \$6.00 per pound during the past 50 years; averaging about \$2.00 per pound. The low of \$1.00 per pound existed for a short time after rich cobalt ores were found in Ontario. The high of \$6.00 per pound was in effect during the postwar boom of 1920-21. In November 1955 the price of cobalt metal (97 to 99 percent, and in 500 to 600 pound containers) was \$2.60 per pound, f.o.b. New York, or Niagara Falls, N. Y. The price of ceramic-grade cobalt oxide (72½ to 73½ percent cobalt, in 350 pound containers) was \$1.98½ per pound west of the Mississippi River (E & M J Metal and Mineral Markets, November 10, 1955, pp. 5-6).

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## COPPER

By J. C. O'BRIEN

About 631,000 short tons of copper have been obtained from deposits in California from 1860 through 1953. This output is dwarfed by the production obtained from the large copper deposits in other western states, but it is valued second only to gold among the metals produced in the state. From 1896, when the Shasta County mines and smelters were first active, to 1930, copper production in California averaged approximately 16,000 tons per year. The low prices of the 1931-36 period, when copper sold from 5.55 to 9.47 cents per pound, caused a severe drop in copper output and the production has exceeded 10,000 tons only in 1944 when the Gray Eagle mine in Siskiyou County and the Mountain Copper Company, Ltd., mine, in Shasta County were active.

The depletion of developed reserves during World War II, coupled with higher operating costs and the necessity of shipping copper ores and concentrates outside of the state for treatment are the principal reasons for the relative quiescence of the copper industry in California during recent years. In 1951 and 1952, despite exploration for copper ore notably in Amador, Calaveras, El Dorado, and Shasta Counties, the production of copper in the state was obtained largely from ores mined primarily for other metals, chiefly zinc and tungsten. The output in 1952 amounted to 800 short tons valued at \$387,200.

In 1952, 92 percent of the total production of copper in California was obtained from three sources—the Afterthought mine in Shasta County, the Penn mine in Calaveras County and the Pine Creek tungsten mine in Inyo County. The balance was recovered from ores mined in Kern, Madera, Nevada, Riverside, San Bernardino and Tulare Counties, and as cement copper precipitated from the mine water at the Hornet-Richmond mine in Shasta County and the New Penn mine in Calaveras County.

**Mineralogy.** Only 16 of about 150 known copper minerals are considered to be of economic importance and six of these have been the source of 95 percent of the copper mined in North America. Copper ores can be conveniently divided into four main groups, the sulfide ores, the oxidized ores, the complex ores, and native copper ores. Most of the world's copper is derived from the sulfide group of which chalcopyrite ( $\text{CuFeS}_2$ ) and chalcocite ( $\text{Cu}_2\text{S}$ ) are the most abundant species. In the United States the sulfide ores yield from 80 to 90 percent of the new copper production.

Chalcopyrite, sometimes designated as "copper pyrite" or "fool's gold," contains 34.5 percent copper when pure. It is brass yellow in color, has a greenish-black streak and is softer than pyrite. It can be distinguished from gold by its greater hardness and brittleness. It tarnishes to a purple sheen. Chalcocite contains 79.8 percent copper when pure and is the most abundant copper mineral in the huge open pit mines in this country. It is a dark lead-gray mineral, can be cut smoothly with a knife, and has a dull black or bluish tarnish which gives it the name of "sooty copper" or "copper glance." It commonly is found as a secondary mineral in the en-

riched sulfide zone of copper deposits, but it also is known to occur as a primary mineral.

Bornite ( $\text{Cu}_5\text{FeS}_4$ ), sometimes called "peacock ore" because of its peculiar purple tarnish, contains 63.3 percent copper when pure. Other sulfide minerals include covellite ( $\text{CuS}$ ), distinguished by its indigo blue color which turns purple when wet; enargite ( $\text{Cu}_3\text{As}_5\text{S}_4$ ), a grayish black mineral which commonly occurs in columnar masses and can be distinguished from stibnite by its darker color; and tetrahedrite ( $\text{Cu}_8\text{Sb}_2\text{S}_7$ ), sometimes called "gray copper" because of its dark iron gray color. Tetrahedrite commonly shows various amounts of iron, zinc, and silver. Massive tetrahedrite can be distinguished from chalcocite because it is brittle and chalcocite is sectile.

The oxidized copper minerals include malachite ( $\text{CuCO}_3\text{Cu}(\text{OH})_2$ ), an emerald green mineral with a pale green streak; azurite ( $2\text{CuCO}_3\text{Cu}(\text{OH})_2$ ), an azure blue mineral with a light blue streak; and cuprite ( $\text{Cu}_2\text{O}$ ) whose color is dark red and brownish red to ruby red.

The green, blue, and red colors of the oxidized copper minerals commonly stain outcrops over extensive areas and suggest that the copper deposits are much larger and richer than they actually are. Such outcrops should be sampled carefully before the development of the deposit is attempted. The oxidized copper ores and native copper have not proved to be of commercial importance in California.

In the copper deposits of California, chalcopyrite is the chief copper mineral; bornite, chalcocite, and tetrahedrite are characteristically subordinate. Pyrite or pyrrhotite and the iron-bearing sphalerite generally are associated with the copper ores. Galena, magnetite, and ilmenite commonly also are present. Malachite, azurite, cuprite, and native copper are found in some deposits, but they have not been important ore minerals. In some deposits chalcopyrite and sphalerite are present, each in commercial amounts, and they must be separated to be marketable. The copper and zinc minerals are so intimately associated in Shasta County that, previous to 1925, deposits containing as much as 16 percent zinc, 2 percent copper and 5 ounces of silver per ton were left as unprofitable to mine. Progress in the technique of selective flotation now makes it possible to make marketable concentrates of both the copper and zinc sulfides from these complex ores. Since 1942, zinc recovered from such ores in California has exceeded the amount of copper recovered.

**Geologic Occurrence.** Most large copper deposits are of hydrothermal origin and are genetically related to igneous rocks. Replacement, in general, has been a more important factor in the formations of deposits than has simple cavity filling. In most deposits, both processes have been active. Deposits, commonly known as the "porphyry coppers," which consist of copper minerals disseminated in extensive alteration zones in granitic rocks, now yield about 75 percent of all of the copper mined in the United States. Such deposits characteristically contain  $\frac{1}{2}$  to 2 percent copper in ore bodies that are measurable in millions of tons to hundreds of millions





FIGURE 1. Outline map of California showing locations of mines that have a recorded production of more than a million pounds of copper each.



## Map list.

California mines that have produced more than a million pounds of copper prior to January 1953, arranged alphabetically by counties.

Map no.	County	Section	Location		B & M
			T.	R.	
	Amador				
1.	Copper Hill.....	34, 35	8N	9E	M.D.
2.	Newton.....	28	6N	10E	M.D.
	Butte				
3.	Big Bend.....	8	21N	5E	M.D.
	Calaveras				
4.	Keystone-Union, North				
	Keystone.....	34	2N	12E	M.D.
5.	Napoleon.....	23	1N	11E	M.D.
6.	Penn.....	3, 4	4N	10E	M.D.
		33, 34	5N	10E	M.D.
7.	Quail Hill.....	3, 10	1N	11E	M.D.
	Fresno				
8.	Copper King.....	3	12S	23E	M.D.
9.	Fresno.....	10	12S	21E	M.D.
	Inyo				
10.	Pine Creek.....	30, 31	6S	30E	M.D.
	Madera				
11.	Daulton.....	35	9S	18E	M.D.
	Nevada				
12.	Spenceville.....	25, 26 27, 35	15N	6E	M.D.
	Placer				
13.	Dairy Farm.....	27	14N	6E	M.D.
14.	Valley View.....	12, 13, 14	13N	6E	M.D.
	Plumas				
15.	Engels.....	3, 4, 5, 8, 10 32, 33, 34	27N 28N	11E 11E	M.D. M.D.
16.	Superior.....	15, 16, 17 18, 19, 20	27N	11E	M.D.
17.	Walker.....	5, 6, 7, 8 29, 30, 31, 32	24N 25N	12E 12E	M.D. M.D.
	San Bernardino				
18.	Copper World.....	6	16N	13E	S.B.
	Shasta				
20.	Afterthought.....	10, 11	33N	2W	M.D.
21.	Balaklala.....	12, 13, 14	33N	6W	M.D.
22.	Bully Hill.....	15, 16, 21 22, 28	34N	3W	M.D.
23.	Hornet.....	35	33N	6W	M.D.
24.	Iron Mountain.....	34, 35	33N	6W	M.D.
25.	Keystone.....	14	33N	6W	M.D.
26.	Mammoth.....	1, 12 32, 33	33N 34N	6W 5W	M.D. M.D.
27.	Rising Star.....	21, 28	34N	3W	M.D.
28.	Shasta King.....	11, 12	33N	6W	M.D.
29.	Sutro.....	29	34N	5W	M.D.
	Siskiyou				
30.	Blue Ledge.....	3	47N	11W	M.D.
		34	48N	11W	M.D.
31.	Gray Eagle.....	13, 14, 23	17N	7E	H.
	Trinity				
32.	Island Mountain.....	9, 10, 15	5S	6E	H.

of tons. They can be mined only by very large-scale open pit methods. Ore is concentrated in huge flotation plants and the copper recovered in nearby smelters. Such operations exist in Arizona, Utah, New Mexico and Nevada, but no mineable porphyry copper deposits have yet been discovered in California.

Copper deposits that have undergone supergene enrichment form a very important group of ores. In these deposits, copper minerals are leached from the zone of oxidation, carried downward in solution, and deposited

below the water table, and thus enrich the primary ores. Some supergene ore is generally present in most copper deposits, but it has been important in only a few of the California deposits that have been developed to date. The possibility of supergene ores at moderate depth beneath the surface must always be considered. A small and marginal grade deposit at the surface may become larger and richer with depth.

*Occurrences in California.* Most of the copper produced in California has been obtained from three districts: one in Shasta County, another in Plumas County, and a third in the Sierran Foothill belt which includes Butte, Yuba, Nevada, Placer, El Dorado, Amador, Calaveras, Tuolumne, Mariposa, Madera and Fresno Counties. Other counties that have contributed significant amounts of copper are Siskiyou, San Bernardino, Inyo and Trinity.

Almost all of the primary copper deposits in California have formed as veins or replacement deposits in igneous or metamorphic rock. Most of the copper deposits in Shasta County consist of chalcopyrite which, with pyrite and sphalerite, has replaced metamorphosed porphyritic rhyolite flows. Some of these deposits are bodies of massive pyrite with chalcopyrite and sphalerite present along their borders. In others the sulfide minerals are disseminated in schist or occur as veins or replacement deposits in schist or limestone.

The copper deposits of Plumas County have formed as hydrothermal alterations of igneous and metamorphic rocks and commonly occur along contacts between two igneous masses or an igneous and metamorphic mass. Tourmalinization of the wall rock is common. Zinc minerals are not abundant.

"The copper deposits of the Foothill belt, of which the most important part is in Calaveras County, are replacement deposits in hydrothermally altered metamorphic rocks, mainly metavolcanics. The ore bodies generally lie along steep faults within or at the contact of silicified, sericitized and pyritized zones. Most of the deposits of the Foothill belt contain both chalcopyrite and sphalerite. The commonly associated metallic mineral is pyrite, but where the metamorphism in the country rock is middle or high-grade, as in Madera County, pyrrhotite is present, in places exceeding pyrite in abundance." (Eric, 1948, p. 209)

The Iron Mountain and Mammoth mines of Shasta County; the Walker and Engels mines of Plumas County; and the Penn and Keystone-Union mines of Calaveras County described in the following paragraphs have been the principal sources of copper in California. The Afterthought mine, Shasta County, and the Penn mine, Calaveras County, were the principal sources in 1952. Smaller lots of copper-bearing ore were also shipped from the Reward mine, Inyo County; the Bagdad Chase mine, Turtle Mountain group, and the Blue Silver mine all of San Bernardino County and from numerous other widely distributed properties. Copper concentrates derived from the Pine Creek tungsten mine, Inyo County, and the Hoffman Estate tailings, San Bernardino County, were marketed in 1952. The Hornet-Richmond mine water, Shasta County, also yielded copper preecipitates.

The Iron Mountain mine, which is owned and operated by the Mountain Copper Company, Limited, is in Shasta



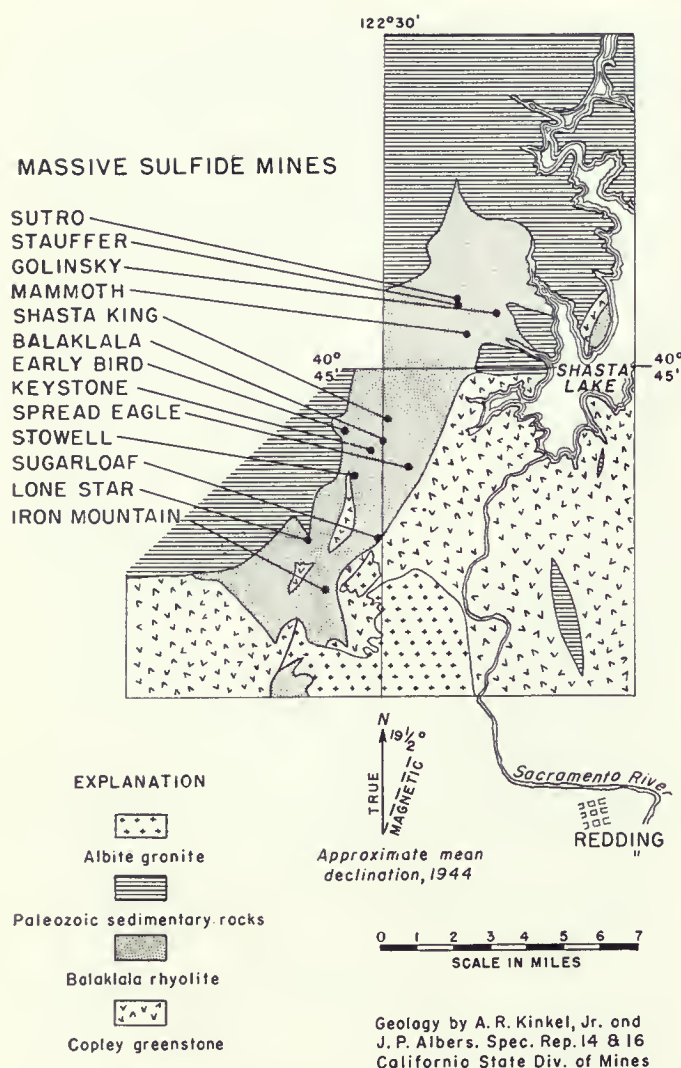


FIGURE 2. Map showing location of West Shasta copper-zinc district and its generalized geologic setting.

County, about 12 miles northwest of Redding. The ore bodies, which lie along a belt that is about  $1\frac{1}{2}$  miles long, are generally lenticular and moderately to gently dipping. They are composed almost entirely of sulfide minerals which occur along zones of breccia in a porphyritic variety of Balaklala rhyolite of Middle Devonian age. The brecciation probably was an effect of the cooling of the rhyolite. The ore-bearing solutions caused the broken rhyolite to be replaced with the massive sulfide deposits which consist mostly of pyrite and also contain chalcopyrite and sphalerite, silver and gold. Within the massive sulfide ore bodies, replacement is almost complete and they are in sharp contact with unreplaced rhyolite. "All the massive sulfide ore contains some copper and zinc, but mineable bodies of copper-zinc ore are closely associated with feeder channels along faults that existed prior to formation of the ore. The ore bodies range in size from a few thousand tons to more than 5,000,000 tons. Tuff and agglomerate layers, which also occur in the rhyolite, appear to have been unfavorable for ore deposition" (Kinkel and Albers, 1951, p. 3).

The development of separate bodies of sulfide ore led to the naming of individual ore bodies as different mines, although they were all mined as one operation by the Mountain Copper Company, Limited. Thus the Old Mine, Number 8, Richmond, Mattie and Hornet mines are separate, and were all worked at different times, but all are part of the Iron Mountain mine. The Mountain Copper Company, Limited, has been mining at Iron Mountain since 1896. It has produced copper from direct smelting ore, from sulfide flotation concentrate, by leaching cinders produced in roasting pyrite for its sulfur content, and by precipitation from mine water. The copper produced from direct smelting ore amounted to 197,951,738 pounds by the end of 1919, but figures are not available for the total copper produced since that date. After 1919 the principal periods of copper production were in 1925, 1928-1930, and 1943-1947. Pyrite has been mined at Iron Mountain since 1907, and since the copper-zinc flotation plant was shut down in 1947 pyrite has been the only ore mined at Iron Mountain (see section on pyrites in this volume).

The Old Mine sulfide lens yielded 1,608,000 tons of massive sulfide ore which averaged 7.5 percent copper, 1.0 ounce of silver, and 0.04 ounce of gold to the ton but this ore was enriched by secondary copper minerals. The zinc content of this ore body is reported by the staff to have been more than 2 percent and may have been as much as 5 percent. A zone of disseminated chalcopyrite underlying the Old Mine massive sulfide lens (the Number 8 mine) yielded eight hundred and twenty thousand tons of ore containing 3.5 percent copper, 0.001 ounce of gold and 0.04 ounce of silver per ton. The zinc content of the disseminated copper ore was very low. About 380,000 tons of ore mined from the Richmond and Mattie ore bodies averaged 2.0 percent copper and 3.5 percent zinc (Kinkel and Albers, 1951, p. 8). Minor copper-bearing sulfides occurred along the borders of the Hornet massive pyrite deposit.

A selective flotation plant built near the portal of the Richmond adit was operated from July 5, 1943 to June 30, 1947 on ore mined from the Richmond and Mattie ore bodies. It produced a copper concentrate that assayed about 13.7 percent copper and a zinc concentrate assaying about 54.65 percent zinc. Many variations in the character of the ore contributed to metallurgical difficulties. Considerable oxidation occurred to the copper minerals along cleavage planes forming some water soluble sulfates, and a high percentage of malachite, which showed a wide range in iron content, contributed to the difficulty in the zinc circuit. (Kett, 1947, p. 141) Nevertheless, an extraction of over 80 percent copper and from 55 to 60 percent zinc was obtained.

Supergene enrichment occurred only in the Old Mine ore body, and residual concentrations of silver and gold minerals were left in the oxidized zone. A large part of this oxidized zone or gossan was mined by means of an open pit between 1929 and 1942 and the gold and silver was recovered by cyanidation. In June 1938, the cyanide plant treated 22,434 tons of ore which averaged 0.0548 ounce of gold and 0.1434 ounce of silver per ton. (Averill, 1939, p. 330) All gossan mining ceased in February 1942.

The Mammoth mine is in the West Shasta copper-zinc district 13 miles northwest of Redding. During its period



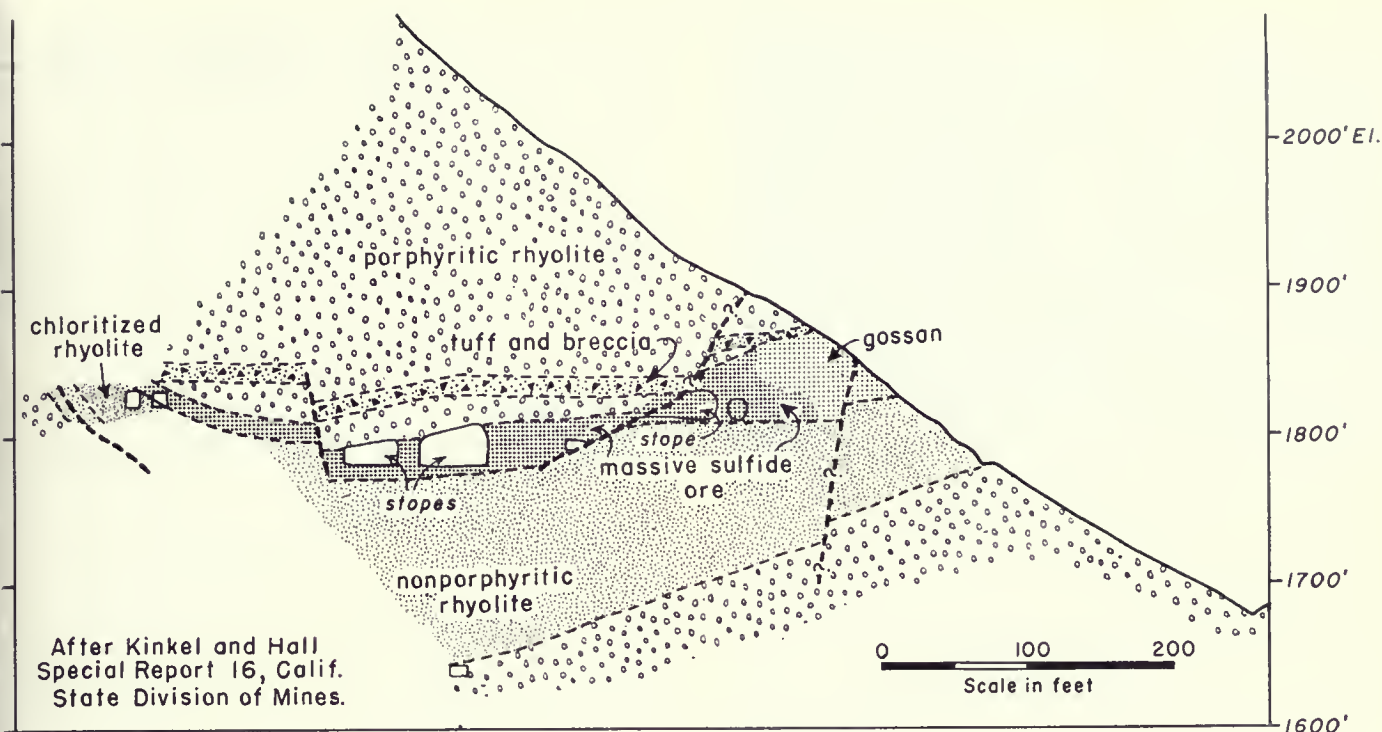


FIGURE 3. Section through Shasta King mine.

of operation from 1905 to 1925, the mine yielded 3,311,145 tons of direct smelting copper ore, and 84,000 tons of high-grade zinc ore (Kinkel and Hall, 1952, p. 3). The ore averaged 3.95 percent copper, 4.62 percent zinc, 0.039 ounce of gold, and 2.32 ounces of silver per ton. The ore bodies are flat-lying and tabular and consist of massive pyrite that contains chalcopyrite and sphalerite and minor amounts of gold and silver. The ore bodies have replaced Balaklala rhyolite of Middle Devonian age along the crest of an elongated domelike arch. They occur at the base of a coarsely porphyritic phase of the rhyolite. The mineralizing solutions centered along pre-mineral faults that acted as feeder fissures. The known ore bodies lie in a zone that trends N. 60° E., is about 4,200 feet in exposed length and is 1,000 feet wide in its central part. Mineable ore bodies occur throughout the ore zone, but the entire zone is not ore. Individual stopes have a maximum horizontal dimension of 900 feet by 500 feet and the maximum thickness of ore is 110 feet.

The United States Smelting, Refining and Mining Company acquired the Mammoth mine in 1904, began large scale mining operations in 1905, and built a smelter at Kennett to recover copper but no provision was made to recover zinc. The mine was worked continuously to 1919, but was closed from 1919 to 1923. Late in 1923, operations were resumed and continued to 1925. No ore has been mined since 1925. Some ore bodies that contained high percentages of zinc were mined and the ore shipped to smelters in the Midwest during World War I and some zinc was recovered in an electrolytic plant in 1917 and 1918. The accumulated flue dust stockpiled at the smelter site was shipped to a smelter in Utah in 1947.

The Walker mine is in Plumas County, about 10 miles southeast of Genesee. For several years after the end of World War I, it was the principal source of copper in

California, but the known ore reserves have been mined out and the property was shut down in October 1941. The ore bodies occurred in wide quartz veins that cut fine-grained, black andalusite-granite schist and cordierite hornfels near the contact of these rocks with intrusive quartz diorite (Eric, 1948, pp. 208-209). The main vein strikes N. 25° to 30° W. and dips from 32° to 70° E. It can be traced on the surface for more than a mile, but the barren white quartz gives little indication of the large ore bodies which lie underneath. Chalcopyrite is the principal ore mineral, but minor amounts of chalcocite and other copper minerals are also present.

The ore occurs as massive bodies of chalcopyrite in the vein quartz, as replacement bodies of chalcopyrite in the wall rock, and as numerous small seams of chalcopyrite that fill shears and fractures in the country rock (Averill, 1937, pp. 96-97). The property has been extensively developed by underground workings and by diamond-drill holes. The 7th level adit, about 900 feet below the outcrop, is the main haulage level. The first 3,000 feet of the adit was driven north through granite. The South ore body was cut at 3,000 feet from the portal and the adit was turned northwest to follow a shear zone. The Central ore body was cut at 3,550 feet, the North ore body at 4,850 feet, the 712 ore body at 8,000 feet, and the Piute ore body at 10,000 feet from the portal. These ore bodies range in length from 600 feet to 1,400 feet and have an average width of about 30 feet.

The shear zones between the ore bodies carry some copper, but are not of commercial grade. The ore was mined by shrinkage stopes leaving pillars to support the back at intervals and to protect the levels. Most of the pillars were recovered later by drilling long holes from service drifts and blasting. Raises were run at 50-foot intervals along the footwall of the ore bodies and from



level to level. The ore bodies beneath the 7th level were mined through two inclined shafts down to the 1,000-foot level and one shaft to the 1,200-foot level. Ore above the 7th level is mostly stoped out.

In 1931, a flotation plant at the mine processed 432,294 dry tons of ore which averaged 1.6317 percent copper, 0.026 ounce of silver and 0.0516 ounce of gold per ton. The concentrate averaged 25.187 percent copper, and 90.49 percent of the copper content of the ore was recovered (Averill, 1937, pp. 102-103). A production of 7,248,128 pounds of copper, 166,581 ounces of silver and 10,938 ounces of gold was reported for 1941 (O'Brien, 1943, p. 80).

The Engels mine is about 15 miles northeast of Greenville in Plumas County. Here, the ore body occurs primarily in diorite, but quartz diorite, microcline aplite and pegmatite dikes also appear in the underground workings. The ore consists of disseminated chalcopyrite and bornite in sheared diorite. These minerals are in roughly parallel bands that give the ore a streaked appearance. These bands parallel the direction of the ore body which trends N. 60° E. with a very steep dip to the north. The shearing appears to be due to rock flowage or flow-cleavage. In the main ore body, the bands may be narrow and scattered throughout the width of the shear zone; but frequently there is a concentration of the ore into one or two bands, one to three feet in width, with a number of small disseminated bands in the remainder of the zone. Magnetite, ilmenite, biotite, hornblende, orthoclase, tourmaline, and quartz are gangue minerals.

The ore body in the Engels mine has been worked to a vertical depth of over 1,300 feet. In its longest part, on the 7th level, it has a length of 800 feet with a maximum width of 100 feet and an average width of 40 to 50 feet.

The mine is developed by a series of 10 adit levels of which Number 10 adit with a length of 8,357 feet is the main haulage level. A shaft sunk from this adit opens up levels 11 to 15. Workings total about 12 miles of drifts, crosscut and raises on 15 levels. Mining was done by shrinkage stoping. Some stopes were as much as 600 feet long, 40 feet wide and 1300 feet high (Averill, 1928, pp. 276-277). The Engels mine had its most active years from 1915 to mid-1930. During that period, 4,692,229 tons of ore were milled from which 161,526,229 pounds of copper were recovered. The presence of gold and silver in the ore added much to its value. The mine and mill have since been dismantled and the property has been idle in recent years.

The Penn mine is in northwestern Calaveras County, about 3 miles northwest of Valley Springs. The ore bodies are sulfide replacement deposits in slightly metamorphosed Jurassic volcanic rocks and in intrusive quartz porphyry. They are associated with alteration zones that show the effects of sericitization, silicification, and pyritization superimposed on the low-grade metamorphic rocks. The ore bodies are steeply pitching lenses at the margins of these zones and along faults within them. Near the Penn mine altered rocks are distributed in six main zones which trend northwestward and as much as 2,850 feet long and 225 feet wide. Their downward extent appears to be at least as great as their length. The ore bodies range in pitch length from 150 to 1,000 feet; in breadth from 100 to 400 feet; and in width

from 4 to 30 feet (Heyl and others, 1948, p. 62). The ore minerals consist mostly of pyrite, sphalerite, and chalcopyrite. Small proportions of bornite, tetrahedrite, and galena are also present. Gangue minerals are barite, calcite, and quartz.

More than 79 million pounds of copper have been produced from the Penn mine since it was first opened in 1861. From December 1943 to the end of 1946 the mine produced 83,555 tons of ore which averaged 2.05 percent copper, 5.58 percent zinc, 7.89 percent lead, 0.07 ounce of gold and 2.37 ounces of silver per ton. The ore was concentrated by flotation and the copper-lead concentrate was shipped to Utah for smelting.

The Keystone-Union, the largest mine in the Copperopolis district of Calaveras County, includes all the underground workings that are appended to the six shafts known, from north to south, as the Keystone-Discovery, Keystone, Union No. 1, Union No. 2, Union No. 3 and South Union (Heyl, 1948, pp. 106-108). These workings lie along a 2,000 foot segment of a mineralized zone which has been developed to a maximum depth of approximately 1,350 feet below the surface. The ore shoots are replacement deposits of chalcopyrite and pyrite in slates and metavolcanic schists of probable Jurassic age. The shoots lie in a zone of intense chloritization that trends N. 38° W. and dips 60° NE. The zone is adjacent to an east-dipping fault that is marked by a well-developed gouge zone. The shoots form a series of irregular, apparently overlapping lenses commonly arranged en echelon. These lenses are composed of interlocking veinlets and irregular streaks and masses of chalcopyrite and pyrite. The boundaries of the ore shoots are vague, and the limits of the mineable materials are determined by assays. The bodies are about 40 feet in maximum width, about 15 feet in average width, and range from 50 to about 400 feet in maximum dimensions. A lenticular mass of granodiorite almost 2,000 feet long and up to 240 feet wide is exposed about 200 feet west of the mine. Granodiorite, however, even where sheared and chloritized, appears to have been less favorable for penetration and replacement by copper-bearing solutions than were slate and schist.

Production from the Keystone and Union mines started in 1861 and by 1869, the properties had yielded 125,739 tons of ore assaying 10 percent copper. The properties were worked intermittently until 1902 when the Keystone and Union mines were combined and operated as a unit. The mine was active in the years 1902-1909, 1911-1920, 1923-1927, 1929-1930 and 1942-1946. The total production, 1861-1946, amounts to about 1,189,000 tons of ore which yielded approximately 72,600,000 pounds of copper.

The United States Vanadium Corporation's Pine Creek tungsten mine at Bishop, Inyo County, has been the chief source of copper in California since 1952. At this mine chalcopyrite is associated with scheelite, molybdenite, silver and gold in ore bodies that lie along the border of a large pendant of metamorphosed sedimentary rocks in granite rock (see sections on tungsten and molybdenum in this volume). The ore body varies in width from 15 to 50 feet and strikes north for an aggregate length of 1,000 feet. The ore averages 0.20 to 0.25 percent copper and a copper concentrate carrying a substantial amount of silver and some gold is obtained as



a by-product from ores mined chiefly for tungsten. Copper is also produced as a by-product from the lead-zinc group of mines at Darwin and the Shoshone group of lead mines at Tecopa operated by the Anaconda Copper Mining Company. At Darwin, chalcopryrite and tetrahedrite occur with galena and sphalerite as limestone-replacement or fissure-filling ore bodies in Paleozoic metamorphic rocks. The ore bodies of the Tecopa district consist mostly of lead carbonate with subordinate galena and chalcopryrite. These have formed as irregular lenses along a gently dipping fault plane in the Cambrian (?) Noon-day dolomite.

At the Bagdad-Chase mine south of Ludlow in San Bernardino County copper is produced as a by-product of gold. In this deposit, a fault breccia of rhyolite and monzonite is cemented with silicious material stained with iron oxides, and copper oxides and copper silicates. The ore averages 0.80 percent copper and 0.262 ounce in gold. The ore is shipped to a smelter in Hayden, Arizona.

*History.* The beginning of the copper industry in California dates from 1860 when Hiram Hughes, searching for gold, found gossan on what was to be the Napoleon mine in the Foothill belt in Calaveras County. He sent some of the ore to San Francisco for assay and it was reported to carry 30 percent copper, worth \$120.00 per ton. For many years the miners, searching for gold, had been throwing away, as worthless rock, rich surface copper ore along the Keystone and Copperopolis lodes. In 1861, small shipments of copper ore were made to Boston and Baltimore and one small lot was sent to Swansea, Wales, by way of New York. The Newton mine was discovered in Amador County in 1861, and several thousand tons of high-grade chalcopryrite ore were shipped before the grade of ore decreased with depth, and mining was no longer profitable. By the spring of 1863, considerable amounts of copper ore were being shipped from deposits near Copperopolis, Campo Seco, and Lancha Plana, in Calaveras County. From 1862-65, Del Norte County ranked second to Calaveras County in the production of copper, and old records show that ore assaying 15 to 18 percent copper was shipped to Germany and Wales for smelting.

Copper was mined at Copper City, Shasta County, then known as Williams, in 1862. In 1863, two hundred and fifty tons of ore was shipped to Swansea, Wales, for treatment. This shipment assayed 8 percent copper, \$40.00 in gold, and \$20.00 in silver, but netted only a small profit. Small quantities of copper ore were shipped from Colusa County to San Francisco from 1862-64. Some of the surface ore was very rich but the grade dropped rapidly with depth. Transportation and smelting costs left very little profit even for the high-grade ores.

The first smelter in California was a small reverberatory furnace built in Contra Costa County in 1862. Coal from the Mount Diablo mines was used for fuel and a matte containing 45 to 48 percent copper was produced. Low-grade oxidized ores were mixed with the sulfides, and the ores were not roasted before smelting. By 1868 there were nine smelting plants operating in the Foothill copper belt. A drop in the price of copper in that year, together with increased cost of mining, and lessened values in depth made copper mining unprofitable and a period of inactivity set in which lasted until 1895.



FIGURE 4. Portal of No. 3 adit and compressor house, Bully Hill mine (Glidden Company). June 1954.

The Iron Mountain property in Shasta County was originally purchased in 1894 by the Mountain Mines, Ltd., an English corporation. The property was in turn acquired by the Mountain Copper Company, Ltd., in 1896. The Mountain Copper Company, Ltd., has been active in mining at Iron Mountain ever since. A massive sulfide deposit was developed beneath a huge gossan outcrop. It was estimated to contain  $1\frac{1}{2}$  million tons of ore averaging more than 7 percent copper and \$2.00 per ton in gold and silver. A smelter was built at Keswick and operated until 1907, after which the ores were shipped to the company's new smelter at Martinez. Many improvements in the metallurgy of sulfide ores and improvements in the design and operation of roasting and smelting furnaces were developed by the Mountain Copper Company, Ltd. Between 1901 and 1908 smelters were built and operated at the Afterthought, Balaklala, Bully Hill, and Mammoth mines in Shasta County.

An increase in the zinc content of the ores together with increasing costs of operation, lower prices for copper and silver, and damage suits for smoke nuisances combined to make copper mining and smelting unprofitable in the Shasta copper belt, and all the smelters were idle by 1919. In this year both the Mammoth and the Afterthought mines were shut down, and Plumas County succeeded Shasta County as the leading source of copper in California. The mines of Plumas County produced a maximum of 26,950,029 pounds of copper in 1925. The Engels and Walker mines were the principal producers. Both properties are now idle and their plants have been dismantled. The mines of Plumas County have produced over 325 million pounds of copper which amounts to about 25 percent of the total produced in California to date. A reverberatory furnace and zinc oxide plant built at Bully Hill in 1933 was operated for about 6 months. The selective flotation plant built at Iron Mountain by the Mountain Copper Company in 1943, produced concentrates of both copper and zinc sulfides until June 30, 1947.

The Coronado Copper and Zinc Company reopened the Afterthought mine at Ingot in 1946, and discovered new ore bodies by diamond drilling. A 100-ton capacity selective flotation plant was built, and mining started in October 1948. The operation continued until July 1949



when the mine was closed down because of the drop in price of copper, lead and zinc. Mining was resumed in July 1950 and continued until August 1952 when the developed ore bodies were mined out. The average assay of all ore mined, October 1948 to January 31, 1951, was approximately 16 percent zinc, 2.7 percent copper, 2 percent lead, 5.0 ounces of silver and 0.04 ounce of gold (Albers, 1953, p. 5).

In June, 1952 the New Penn Mines, Inc. took over a lease and option to purchase agreement on the Penn mine at Campo Seco in Calaveras County. A flotation plant on the property was remodeled and its capacity increased to 200 tons per day. Mining was done through the No. 2 and No. 3 shafts between the 500 and 1,000 foot levels, mostly toward the south. A zinc concentrate carrying as much as 2 percent copper was shipped to Amarillo, Texas, and a copper concentrate carrying as much as 10 percent zinc was shipped to Tacoma, Washington. Mining was stopped in January 1953 and a diamond drilling exploration program was started. Holes were pointed northwestward from the 1,100 level of the No. 3 shaft in a search for an ore body beyond the Campo Seco fault.

Other activities early in 1953 included the re-opening of the Number 3 adit at the Bully Hill mine in Shasta County to drive toward ore bodies discovered by a diamond drill exploration project, and the unwatering of the Noonday Copper mine in El Dorado County for exploration under a purchase contract. The Providence Tuolumne Gold Mining Company was granted a government loan to extend the adit at the Copper Bluff lease on Hoopa Reservation in Humboldt County, to search for a faulted block of ore.

*Mining Methods and Treatment.* The cost of developing a copper prospect into an operating mine is usually beyond the financial capacity of individuals or small companies. Few copper deposits are rich enough to ship to smelters without milling and it may cost several hundred thousand dollars and a year or more in time to develop enough ore to justify the construction of a flotation plant.

The physical characteristics of a copper deposit and the percentage of copper it contains determine the method of mining. Profitable exploitation of low-grade ores is achieved by: (1) large scale, open-pit methods using power shovels, bulldozers, pull-type scrapers, dump trucks, belt conveyors or locomotives with trains of large capacity cars; or (2) underground methods using large scale glory-hole or block-caving methods with haulage and hoisting facilities able to handle large tonnages. The average tenor of copper ores mined in 1953 in the United States was 0.85 percent when the average price of copper was 28.92 cents per pound. More than 80 percent of the copper ore mined in the United States is taken from open pits.

Sulfide ores now being mined by large scale underground methods contain as little as 0.75 percent copper. The "porphyry" type deposits have not been found in California. High-grade sulfide ore in veins mined by underground methods may contain as little as 3 or 4 percent copper. Oxidized ores containing about 1 percent copper are now being mined in the United States, and the copper is recovered by leaching. Ores carrying

5 percent or more copper are generally smelted directly to avoid concentration losses unless they contain an excessive amount of zinc, arsenic or antimony or the distance from the deposit to the smelter is too great. California copper ores with less than 3 percent copper are generally concentrated before smelting.

All of the California copper deposits are mined by underground methods. The principal mines are developed by shafts or adits with haulage levels at convenient intervals. Raises are run in the ore along the footwall from level to level. In some mines pillars are left in the stopes to support the back, but square sets and filling are used to mine high-grade ore. Compressed air shoveling machines are used in the drifts and cross cuts in the larger mines. Power scrapers are used in flat stopes to scrape the broken ore into chutes or cars. The ore is loaded into mine cars, and trains of cars are hauled by electric locomotives to the shaft or to mill ore bins.

All the copper ore mined in California in recent years has had to be concentrated before shipping to a smelter. In many deposits chalcopyrite is so intimately mixed with sphalerite that very fine grinding is required to effect a separation of these minerals, and selective flotation is required to produce concentrates acceptable to the copper and zinc smelters.

Flotation is a method of wet concentration. When finely ground sulfide ore, mixed with water, is agitated and aerated with small amounts of certain oils and certain organic chemical compounds, some of the oil and most of the organic compounds adhere to the mineral particles and float them to the surface where they are skimmed off as a concentrate. The gangue minerals remain submerged and can be diverted to waste.

When two or more minerals are floated together to form one concentrate, the process is known as bulk flotation. Selective flotation employs one of two methods: (1) one or more of the sulfide minerals are depressed during flotation of one or more other minerals, or (2) several different sulfides are floated successively. Milling plants in California commonly yield (1) a copper-lead concentrate which includes the gold and silver, and (2) a zinc concentrate. The concentrates are shipped to smelters in Arizona, Montana, Texas, Utah, or Washington. Flotation can make marketable concentrates from complex ores, but the fine grinding required for most ores is costly and much of the copper and zinc is lost in the process. Zinc concentrates commonly assay 1.5 to 2 percent copper and copper concentrates assay from 5 to 10 percent zinc which is not paid for by the smelter. The freight paid in shipping the concentrates to smelters in Arizona, Montana, Texas, Utah, or Washington is an additional handicap to California mines.

Recent developments in fluosolids roasting suggest that a bulk sulfide concentrate could be roasted, then leached and the metals recovered electrolytically, by-passing the smelter entirely. Sulfur, which could be recovered in the process, should also find a profitable market on the West Coast.

Pyritic ores containing economic quantities of zinc and copper or lead are common, and the general scheme for treating them by flotation is somewhat standardized. Pyrite and sphalerite are depressed with cyanide and other reagents such as zinc sulfate; the copper minerals are floated in a neutral circuit with a collector; sphal-



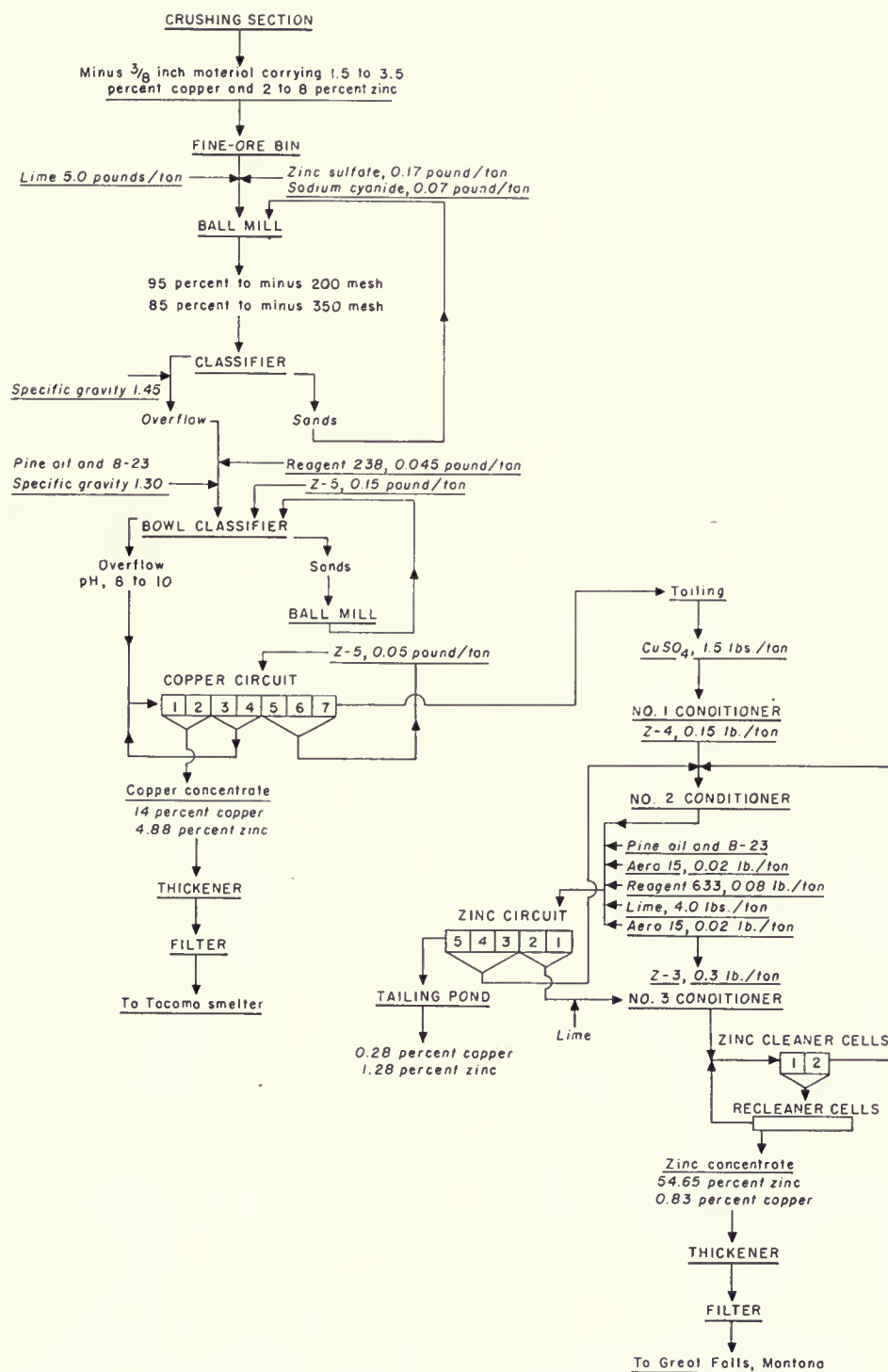


FIGURE 5. Flowsheet of the Mountain Copper Company, Ltd., flotation plant at Iron Mountain, June 1944, by E. M. Bagley, Mill Superintendent.



Table showing recovery of copper and zinc at three California flotation plants.

(Bramel, 1948, p. 163.)

Mine	Product	Weight percent	Analysis percent		Recovery percent	
			Copper	Zinc	Copper	Zinc
Big Bend (Surcease)-----	Mill feed	100.	2.01	12.55		
	Copper concentrate	5.26	25.2	10.9	66.0	4.6
	Zinc concentrate	21.81	2.58	52.6	28.1	91.4
	Tailing	72.93	.162	.68	5.9	4.0
Penn (Eagle Shawmut)-----	Mill feed	100.	2.43	12.0		
	Copper concentrate	8.53	22.58	13.23	79.10	9.41
	Zinc concentrate	19.70	1.16	52.43	9.38	85.98
	Tailing	71.77	0.39	0.77	11.52	4.61
Iron Mountain (The Mountain Copper Company, Ltd.)-----	Mill feed	100.	2.28	4.54		
	Copper concentrate	14.50	11.98	4.26	76.20	13.61
	Zinc concentrate	5.08	1.46	49.10	3.26	54.99
	Tailing	80.42	0.58	1.77	20.54	31.40

erite is activated with copper sulfate in a high-lime circuit for the depression of pyrite; and the zinc minerals are floated with a selective collector and a selective frother. One to three stages of cleaning are common.

The flotation plant of the Mountain Copper Company, Ltd., recovered as much as 88.5 percent of the copper and 54.99 percent of the zinc in a massive pyritic ore, but the extraction was much lower on ore blasted and exposed to the air for more than a week. Success depended on fresh ore and keeping the alkalinity low. As a rule, a pH of 8 to 10 was maintained in the copper circuit. It was found necessary to heat the zinc circuit to 80 degrees Fahrenheit to obtain a shipping grade of at least 47 percent zinc. A high percentage of marmatite (sphalerite containing 10 percent or more of iron) contributed to the difficulty in the zinc circuit.

**Smelting.** At the copper smelter, the copper concentrate, which usually contains from 20 to 35 percent copper, is roasted in a multiple hearth furnace to burn off the excess sulfur together with arsenic, antimony, and other impurities. The resulting calcine is smelted in a reverberatory furnace to produce an artificial sulfide of copper and iron called "matte." The gold, silver, and certain other metals contained in the ore are collected in the matte. Most of the material in the gangue is contained in the slag which floats on top of the matte in the reverberatory furnace and is skimmed off. The matte settles to the bottom of the furnace and is tapped into ladles and transferred to a converter.

Convertors are barrel-shaped containers made of steel and lined with magnesite brick. They are mounted on trunnions so that they can be tilted and their contents poured into ladles. As soon as the matte is poured into a converter, compressed air is introduced through tuyers located on each side of the converter near the bottom. The impurities in the matte are oxidized and converted either into gases which pass off in the flue system, or into slag which can be removed before the copper itself

is oxidized. The oxidation of the sulfur and iron produces enough heat to maintain the materials in a molten condition. The iron oxide and silica combine to form slag which is poured into ladles. The copper sulfide separates from the matte and settles to the bottom of the converter where it is converted into blister copper by oxidation of the remaining sulfur. Blister copper, which is about 98.8 percent pure, is poured into ladles which are emptied into refining furnaces where the remaining impurities are burned out by blowing air through pipes inserted through side doors and plunged into the molten mass. The oxidized copper is brought back to metal by plunging wooden poles into the molten copper. Oxygen combines with the carbon of the wood and passes off as gas. Copper is tapped from the refining furnace into anode shapes for electrolytic refining.

**Price.** In February 1953, when the Office of Price Stabilization decontrolled the prices on all non-ferrous scrap and on primary copper, the average price for domestic copper advanced from the controlled price of 24.2 cents per pound to 29.289 cents per pound by March. The price of foreign copper which was quoted at 34.783 cents per pound in February 1953, under the National Production Authority formula, dropped to 29.71 cents per pound in May when all government controls were removed. The average price for domestic copper in 1954 was 29.694 cents per pound and export or foreign copper averaged 29.889 cents per pound. In September 1955, the average price for electrolytic domestic refinery copper was 44.052 cents per pound and export copper averaged 44.339 cents per pound (Engineering and Mining Journal quotations).

The principal market for refined metals in the United States is in the vicinity of New York City. Market quotations generally refer to the price the industrial buyer is willing to pay for the metal in desirable shapes at the refineries near New York. Refined lead and copper, however, are available on the West Coast in quantity, being



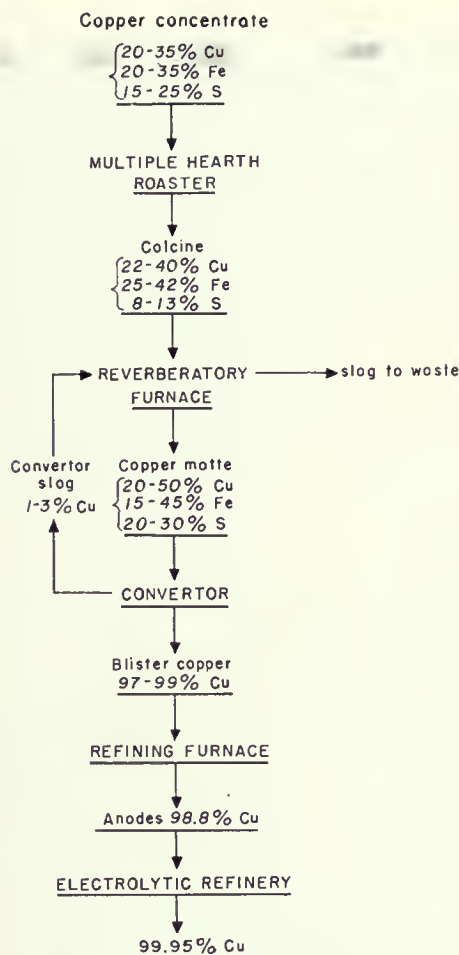


FIGURE 6. General flowsheet for the smelting of copper sulfide concentrates.

derived largely from smelting of imported ores. Lead ore is smelted at Selby, California, and copper ore at Tacoma, Washington.

The rapid growth of population and industries in California has created an expanding market for copper in all its forms. The California copper deposits are very seriously handicapped however, because all of their ores and concentrates must now be shipped out of the state for smelting and refining. Much of the copper produced in the state travels as far as the Atlantic Coast before it returns in the form of copper wire, sheets, or tubing, or in brass and bronze bushings and bearings to be used in buildings, machines, and equipment built in California.

**Utilization.** Next to iron, copper is the most important metal in our modern civilization. In its electrical and thermal conductivity, copper ranks second to silver. Its ductility, malleability, and resistance to corrosion have led to its application in many domestic and industrial uses. Although aluminum, galvanized iron, stainless steel, silver and certain plastics can be substituted for copper in some of its present applications, the demand for copper probably will increase. The electrical industry uses enormous quantities of copper each year in the form of wires, cables, bars and various fittings. Because of its high thermal conductivity, copper is used

in heat-transfer units such as cooling fins, and copper tubing in radiators, fireboxes of locomotive boilers, steam pipes, and radiant heating panels. Large quantities of copper tubing for water pipes also are used in buildings and in the manufacture of household appliances such as refrigerators and air conditioning units. Thousands of tons of copper are used annually in the production of alloys such as brass, bronze, bell metal, gun metal, monel metal, and constantan. Copper oxide and various salts are used as coloring agents in paints, glasses and ceramic glazes. Other copper salts are used for chemicals, antiseptics and insecticides.

Copper sulfate ( $\text{CuSO}_4$ ), containing about 40 percent copper, is the most important copper compound. It is used as a fungicide, as a source of mineral in fertilizers, as a depressant and dispersion agent in flotation plants, in dyes, galvanic cells, photography, antiseptics and in the manufacture of crayons. Production of copper sulfate in 1953 amounted to 72,188 short tons of which 19,872 tons were used in agriculture, 18,000 tons in industry and 34,316 tons for other uses, chiefly for export. Other copper compounds such as copper oxides, chlorides, carbonate, nitrate, and acetate are used in lesser amounts in chemical, paint, electroplating and other industries.

Wire mills are the chief consumers of refined copper and account for over 50 percent of the total production. Brass mills account for about 48 percent and the remainder is used in foundries, secondary smelters, chemical plants and miscellaneous industries.

**Copper Alloys.** Copper is alloyed with a great many elements and in many proportions to obtain metals with desirable properties. The most common alloys are the copper-zinc group, known as brass, and the copper-tin group, known as bronze. Other common alloying elements with copper are lead, nickel, aluminum, manganese, silicon, beryllium, phosphorus and arsenic. A combination of two or more elements is often used in copper alloys. A small amount of lead in brass, for instance, improves its machining properties and a small amount of silicon in bronze improves its corrosion resistance and tensile strength. A variety of nickel-copper alloys are used where a bright corrosion-resistant metal is desirable such as for kitchen, hospital and chemical plant equipment. Beryllium-copper alloys containing 2 to 4 percent beryllium are used where fatigue resistance, hardness, toughness, low sparking, tensile strength and nonmagnetic properties are important such as for springs, nonsparking tools, molds, and aircraft parts.

Aluminum alloys containing about 4 percent copper and fractional percentages of silicon and magnesium have the strength and hardness of mild steel. Copper-steel alloys are used where resistance to corrosion is needed and the cost of chromium steel is not warranted. Gold and silver used for coins, jewelry and silverware are alloyed with copper to increase their hardness, toughness and wearing qualities.

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FIGURE 7. Penn mine, Campo Seco, Calaveras County. Photo by Mary Hill.



## QUOTATION NO.

## DOMESTIC PURCHASE SCHEDULE

## EFFECTIVE DATE

Shipper Tentative Schedule

Address

Mine

Location

Character of Product Copper Concentrates Shipping Point

The following purchase terms are subject to the General Clauses shown on the back of this sheet, and are subject to prompt acceptance. Unless shipments are begun within 30 days, this quotation is automatically cancelled.

TONNAGE: Limited to 500 tons per month except by special arrangement.

DELIVERY: F.O.B. cars at unloading bins, or F.O.B. wharf of the Smelter, Washington.

DATE OF DELIVERY: Date upon which the last car of each lot is accepted by Smelter, or upon which carrying vessel commences discharge of product on Smelter wharf.

PAYMENTS

**GOLD:** (A) If 0.03 of a troy ounce per net dry ton and less than 3.00 ounces pay for all at 91.14%, (B) If 3.00 ounces and less than 5.00 ounces pay for all at 92.57%, (C) If 5.00 ounces and less than 10.00 ounces pay for all at 93.29%, (D) If 10.00 ounces or over pay for all at 94.00%, at the net price per ounce paid by the United States Mints for gold recovered from domestic mine production on the fifteenth day following delivery of the product to the Tacoma Smelter. Nothing paid for gold if less than 0.03 of a troy ounce per net dry ton.

(Note: At the present government price the above terms are equivalent to paying for 100% at the following prices: (A) \$31.81663, (B) \$32.31663, (C) \$32.56663, (D) \$32.81663)

**SILVER:** Pay for 95% at the realized Mint price (i.e., Mint price less Buyer's deductions to cover delivery and other expenses), provided the silver content qualifies for Government purchase and necessary affidavit or other proof is furnished, or, if higher, at the average Handy and Harman New York silver quotation for the calendar week including the date of delivery. Minimum deduction One-Half troy ounces per net dry ton. The present realized Mint price is 90¢ per ounce.

**COPPER:** Deduct from the wet copper assay One unit and pay for 100% of the remaining copper at the daily net refinery domestic quotations for electrolytic wirebars, as published in the E. & M. J. Metal and Mineral Markets of New York averaged for calendar week including date of delivery, less a deduction of Three cents per pound of copper accounted for. Nothing paid for copper if less than One % by wet assay.

No payment will be made for any metal or content except as above specified.

DEDUCTIONS

**BASE** \$ 13.85 per net dry ton of 2,000 pounds, provided the sum of payments for gold, silver and **CHARGE:** copper does not exceed \$ 100.00 per net dry ton. Add to the base charge Ten percent of the excess over such payment of \$ 100.00 to a maximum base charge of \$ 17.50 per net dry ton.

**SILICA:** For ores of a siliceous character, add to the base charge --- cents for each unit deficiency in available silica below, --- per cent; fractions in proportion. To determine available silica deduct two-thirds of the iron assay from the silica assay.

**ZINC:** 5% free. Charge for the excess at 30c per unit; fractions in proportion.

**ARSENIC:** 1% free. Charge for the excess at 50c per unit; fractions in proportion.

**ANTIMONY:** 1% free. Charge for the excess at \$1.00 per unit; fractions in proportion.

**NICKEL:** 0.5% free. Charge for the excess at \$3.00 per unit; fractions in proportion.

**MOISTURE:** A minimum deduction of 1% will be made from wet weight; when over 1% contained, actual moisture will be deducted. Moisture in excess of 10% will be charged at 10c per unit; fractions in proportion.

**TAXES,  
SHIPMENT**

**AND FREIGHT:** See Clauses 1, 5, 6 and 12 on reverse side of this schedule.

By \_\_\_\_\_

"A typical smelter schedule."



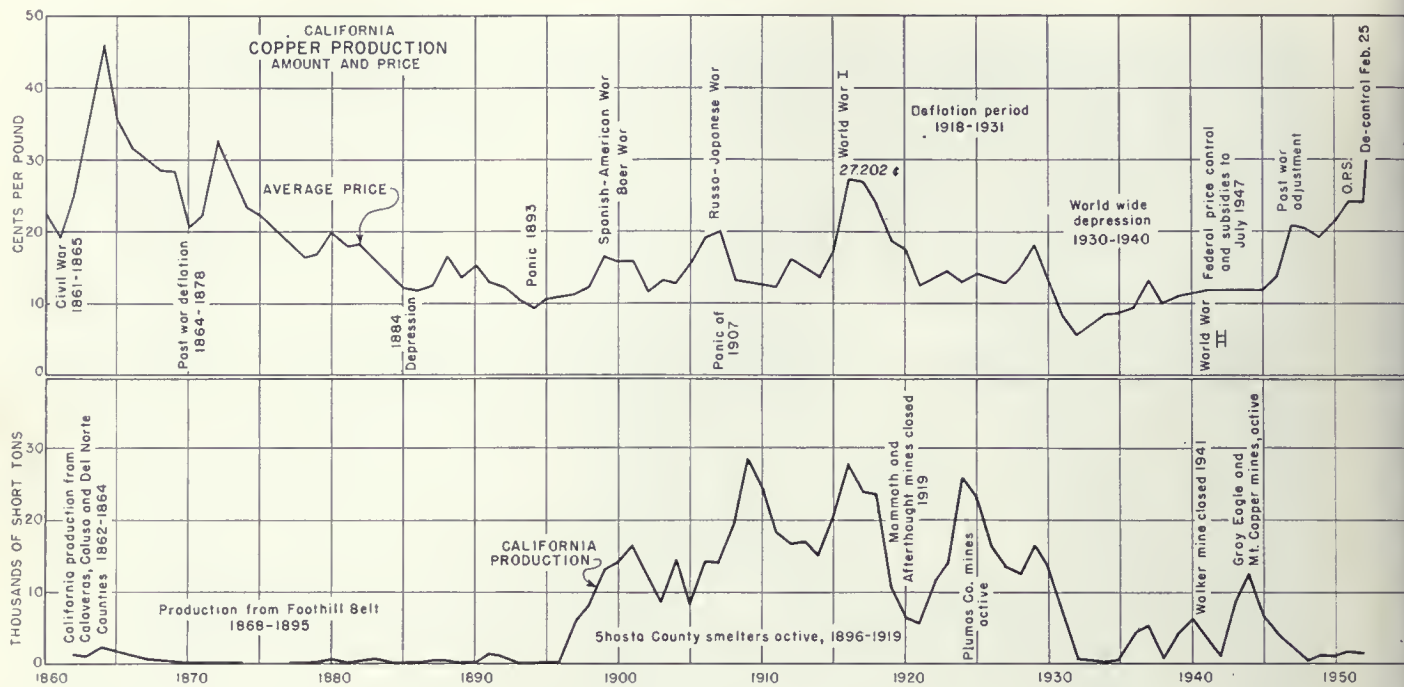


FIGURE 8. Chart showing production of copper from California mines and price of copper in the United States, 1860-1954.

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## DIATOMITE

By GORDON B. OAKESHOTT

The use of diatomite (diatomaceous earth), especially for filtration and in fillers, has been increasing rapidly in the past few years. Production in California has more than doubled in the last 15 years; production for 1953-55 increased 20 percent over that of 1950-52. California is the principal diatomite-producing state and contains the world's largest diatomite quarries near Lompoc in Santa Barbara County.

### GEOLOGIC OCCURRENCE

Diatomite is a light-colored, light-weight sedimentary rock composed largely of the microscopic tests of diatoms. Diatoms are silica-secreting single-celled plants, of which more than 25,000 species are known (Hanna, 1951); 200 to 300 species have been identified in the deposits at Lompoc in Santa Barbara County. These vary widely in form, but disc-shaped and needle-shaped forms are most common. Radiolaria, silico-flagellates, and sponge spicules are other common siliceous organisms found in some diatomite.

Diatomite can be tentatively identified in the field or in hand specimen by its light color and extreme lightness of weight. It is most easily confused with some types of volcanic ash, but microscopic examination permits a ready distinction between the glass particles in volcanic ash and the diatom tests of diatomite. Some diatoms are too small to be recognized as such by the use of the ordinary hand lens (magnification 14X), but diatoms can be seen by this means in most California diatomite.

In California the marine diatomaceous shales, of the upper Miocene and lower Pliocene epochs, are notable also for perfectly preserved fossil fishes; in some places shark teeth, whale bones, and fossil birds have been found. Impure varieties of diatomite contain clay, silt, fine sand, limestone, thin beds of volcanic ash, and hard silica rock, including opal and opaline and porcelaneous chert materials. Commercial grades of diatomite contain less than 15 percent of such impurities. Every gradation is found, from nearly pure diatomite through diatomaceous shale into clay shales and siltstones. Some varieties of diatomite are partly calcareous in that they contain foraminifera.

Lenses, nodules, and layers of porcelaneous silica rocks, and opaline and chalcedonic cherts are common in even the purer forms. Numerous phosphatic nodules or pellets and thin beds of silvery volcanic ash may also occur in certain stratigraphic positions. Many diatomaceous beds grade laterally into chert beds and also grade into coarse clastic sediments.

Diatomaceous rocks, such as those of the upper Miocene and lower Pliocene formations in California, are now known to be of shallow-water origin. These rocks formed with clastic sediments under conditions that allowed diatom tests to accumulate in greater volume than the clastic material. Bramlette (1946) has recently discussed the origin of diatomite and other siliceous rocks of the Monterey formation. He believes that the silica needed to form the large quantities of diatoms originated in the finely divided particles of volcanic ash so commonly associated with beds of both marine and fresh-water diatomite.

In general, geologists mapping diatomite in California find it useful to recognize three types of diatomite—pure, thinly stratified; impure, coarsely stratified; and impure, massive. The apparently pure, thinly stratified beds are of greatest commercial interest, but the suitability of each stratum exposed in an operating quarry must be determined only by actual testing of the product.

In California, the diatomite of actual or potential commercial importance is found in sedimentary rock formations of two different modes of origin: (1) the marine upper Miocene Monterey formation including its equivalents by other names, and the lower Pliocene Siquoc formation, and (2) fresh-water lake beds of Tertiary and Quaternary age. The first group, by far the more important, has yielded nearly all of the diatomite produced in the state. The Monterey formation is widely exposed throughout the Coast Ranges from Point Arena in Mendocino County southward to San Onofre in San Diego County, and extends eastward into the San Joaquin Valley. Diatomite is a common rock type in this formation. Thicknesses of diatomite of as much as 1,000 feet occur in the Siquoc formation of the Santa Maria Basin and Santa Ynez Mountains in Santa Barbara County. In eastern and northern California numerous fresh-water deposits of diatomite have been found in lake beds of Tertiary and Quaternary age. These are associated with volcanic rocks. Diatomite also occurs in some marine Eocene and Cretaceous formations in the Diablo Range.

There is no significant difference in the commercial value and application of marine and freshwater diatomite. The diatomite mined in California is obtained almost wholly from Tertiary marine strata, but Nevada's large production comes from fresh-water Tertiary strata.

*Upper Miocene and Lower Pliocene Deposits.* The foothills of the Santa Ynez Mountains south of Lompoc Valley and the Santa Rita Hills, both in Santa Barbara County, comprise an area that contains what are often regarded as the most extensive deposits of commercial diatomite in the world. Johns-Manville Products Corporation, which in 1953 celebrated the 60th anniversary of the first shipment of commercial diatomite in California, operates huge quarries 3 miles south of Lompoc. The other major diatomite operator in California, Dicalite Division of Great Lakes Carbon Corporation, works a similar deposit 7 miles southeast of Lompoc. Both of these deposits, which are probably correlative, are of marine origin and belong to the Siquoc formation of uppermost Miocene (?) to lower Pliocene age. Their geologic occurrence (fig. 2) has been mapped and described by Dibblee (1950). The best grade of commercial diatomite is in the lower part of the Siquoc formation. A report of the U. S. Geological Survey by Woodring and Bramlette (1950) describes and shows the location of diatomite beds in the Siquoc formation in the Santa Maria district north of the area mapped by Dibblee. These two papers constitute the best guide to the location of the diatomite deposits of commercial grade in the coastal regions of central and southern California.



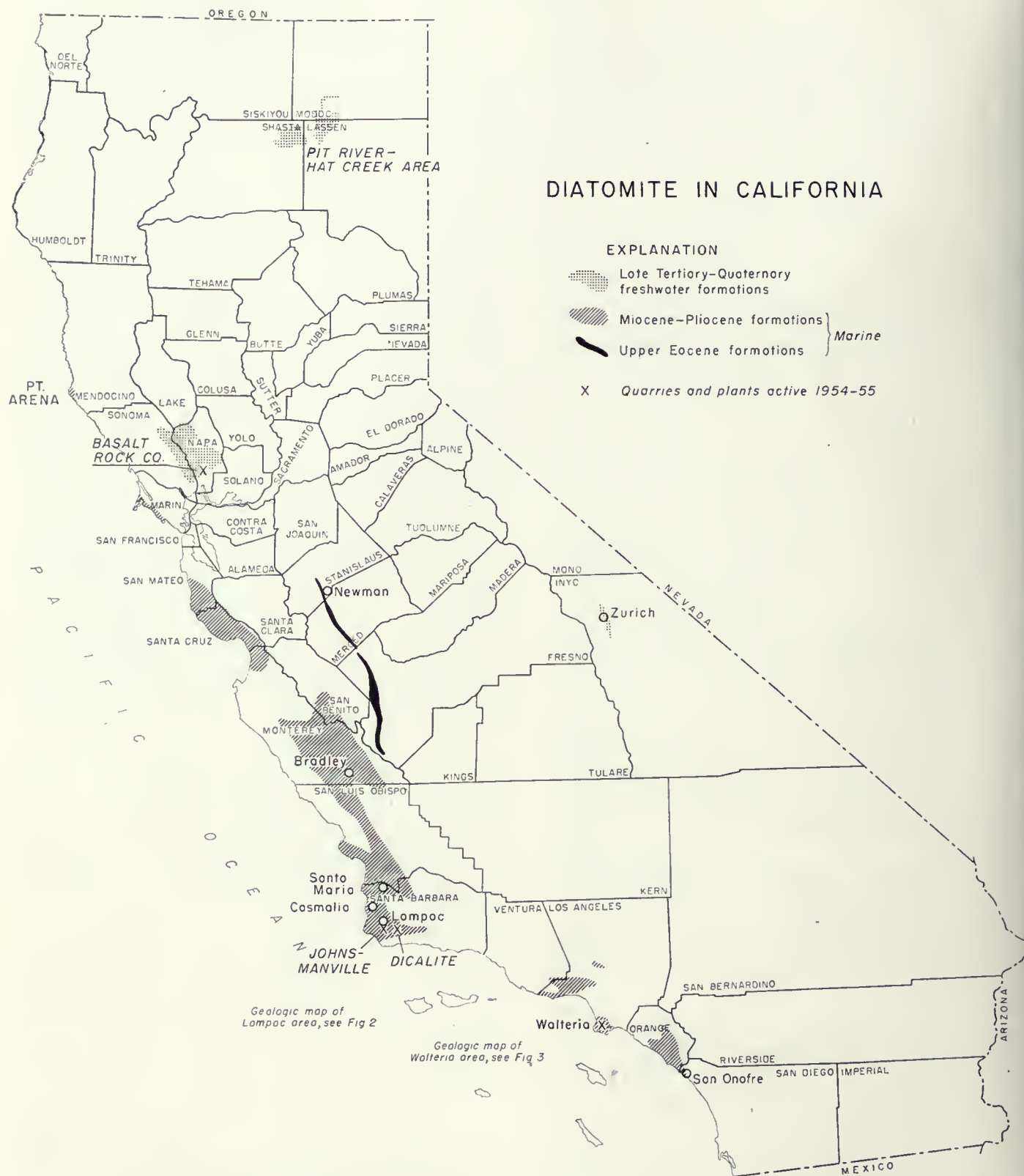


FIGURE 1. Map of California showing the generalized distribution of formations that may contain diatomite.



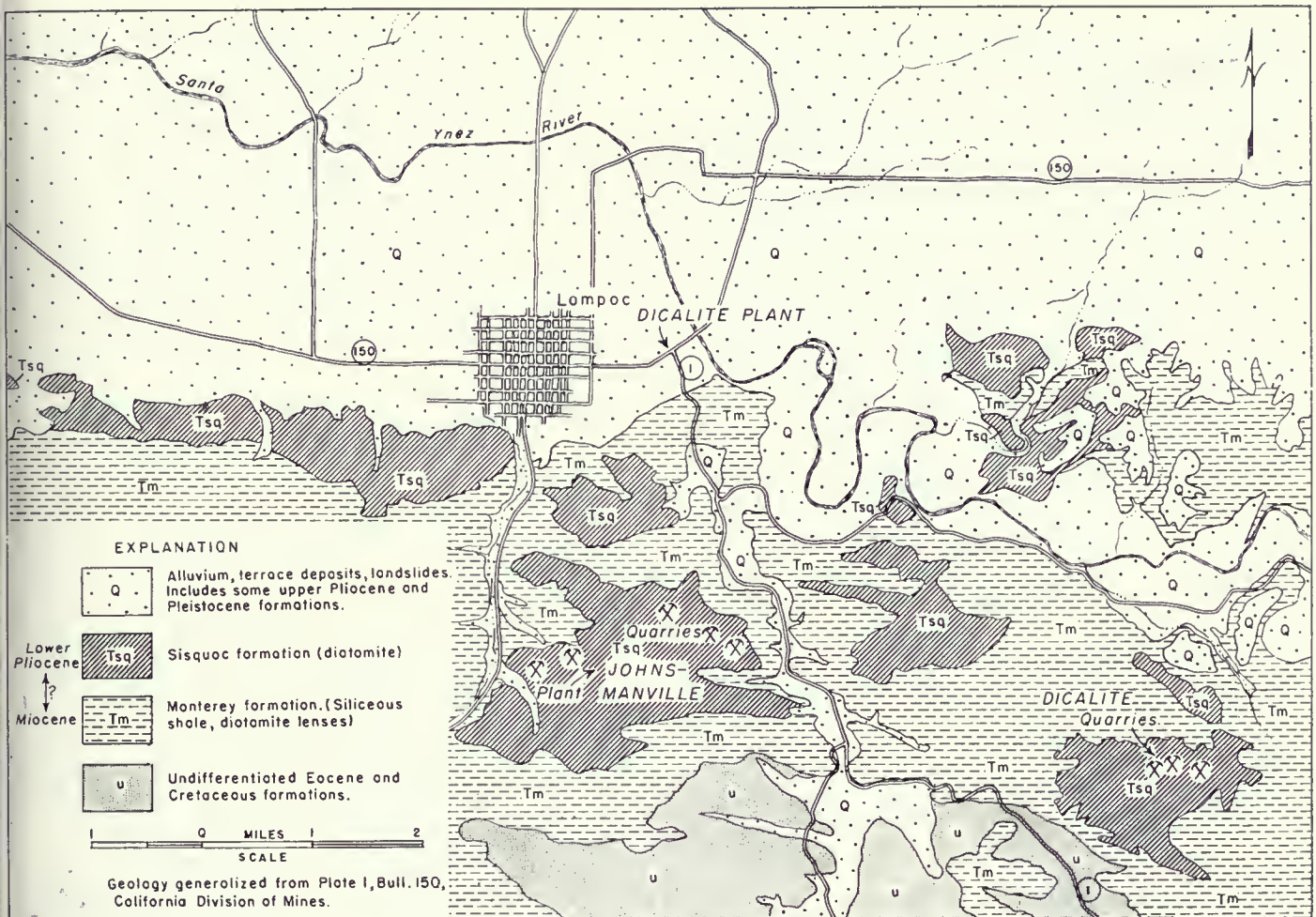


FIGURE 2. Geologic map of the Lompoc area, Santa Barbara County, showing distribution of the diatomite-bearing Sissoo formation. After Dibblee, 1950.

Dicalite Division of Great Lakes Carbon Corporation also operates a large commercial deposit of diatomite in marine beds of the upper Miocene Valmonte diatomite member of the Monterey formation on the north side of the Palos Verdes Hills, near Walteria, in Los Angeles County. A paper by Woodring, Bramlette, and Kew (1946) includes a description and map of the Valmonte diatomite (fig. 3).

Extensive diatomite deposits also occur in Hames Valley 5 miles northwest of Bradley in the southern Salinas Valley and continue northward for several miles from that locality. These have not been worked for many years.

**Other Deposits.** The marine sedimentary Kreyenhagen formation of upper Eocene age extends as a narrow belt in the foothills along the west side of the San Joaquin Valley, northwest from the Coalinga district. This formation contains a great deal of diatomite of possible commercial importance. It has been worked, for example, at the mouth of Panoche Creek, and west of Crows Landing.

In the Panoche Hills on the west side of the San Joaquin Valley the oldest known diatomite in California is found in the upper part of the marine Upper Cretaceous Moreno formation. About 200 feet of buff dia-

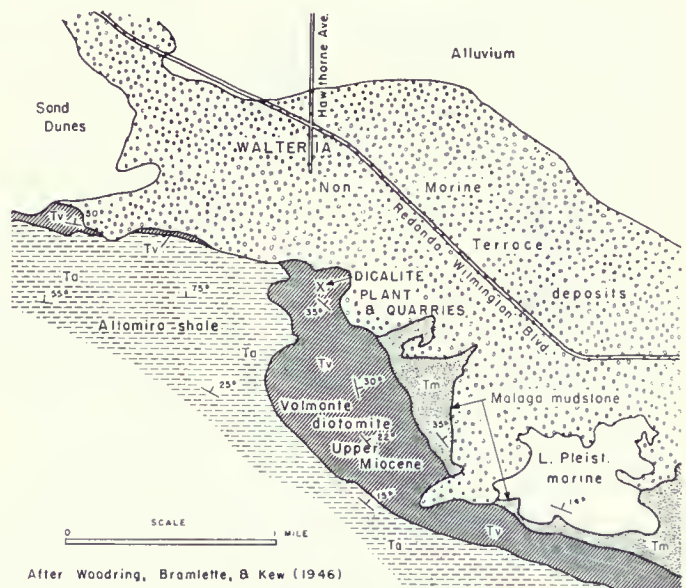


FIGURE 3. Geologic map of the north side of the Palos Verdes Hills. The upper Miocene Valmonte diatomite (Tv) is overlain by Malaga mudstone (Tm) and underlain by Altamira shale (Ta). After Woodring, Bramlette, and Kew.



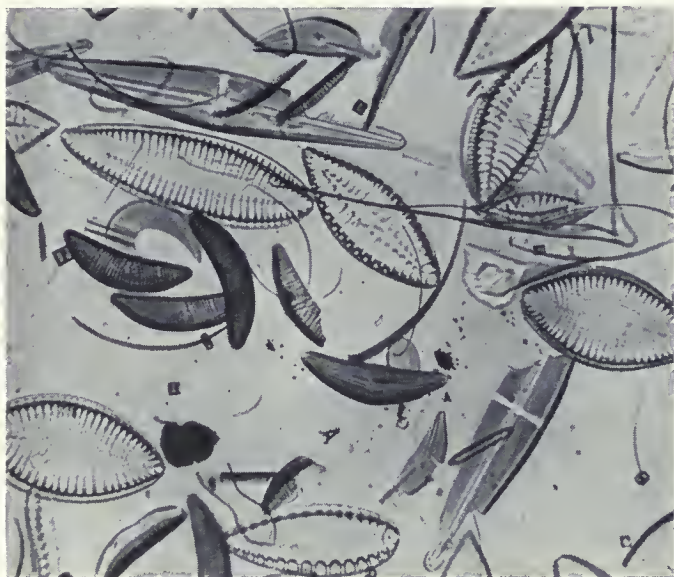


FIGURE 4. Species of diatoms common in fresh-water deposits. Average diameter of the fossils is about 0.05 mm. Photo courtesy P. W. Leppla.

tomaceous shale were sampled and the diatoms described by Hanna (1927 and 1951). The beds are not of present commercial interest but demonstrate the existence of marine diatoms of far greater age than is ordinarily recognized.

Freshwater diatomite, formed in late Tertiary and Quaternary lake beds and interbedded with lava flows and volcanic ash, is widely distributed through parts of Inyo, Shasta, Siskiyou, and Modoc Counties. Such deposits have been worked on a small scale near Tinemaha Lake, 14 miles south of Zurich in Inyo County, and along the Pit River in Shasta County. Those near the junction of the Pit River and Hat Creek are several hundred feet thick; they were described by Logan (1926).

#### PRINCIPAL COMMERCIAL OPERATIONS

Some effort toward the commercial production of diatomite has been made in Contra Costa, Fresno, Inyo, Kern, Monterey, Napa, Orange, Plumas, San Benito, San Joaquin, San Luis Obispo, Shasta, Sonoma, and Tehama Counties. Five producers were listed for the state in 1947; by 1954 only the extensive deposits operated by Johns-Manville Products Corporation and Dicalite Divi-

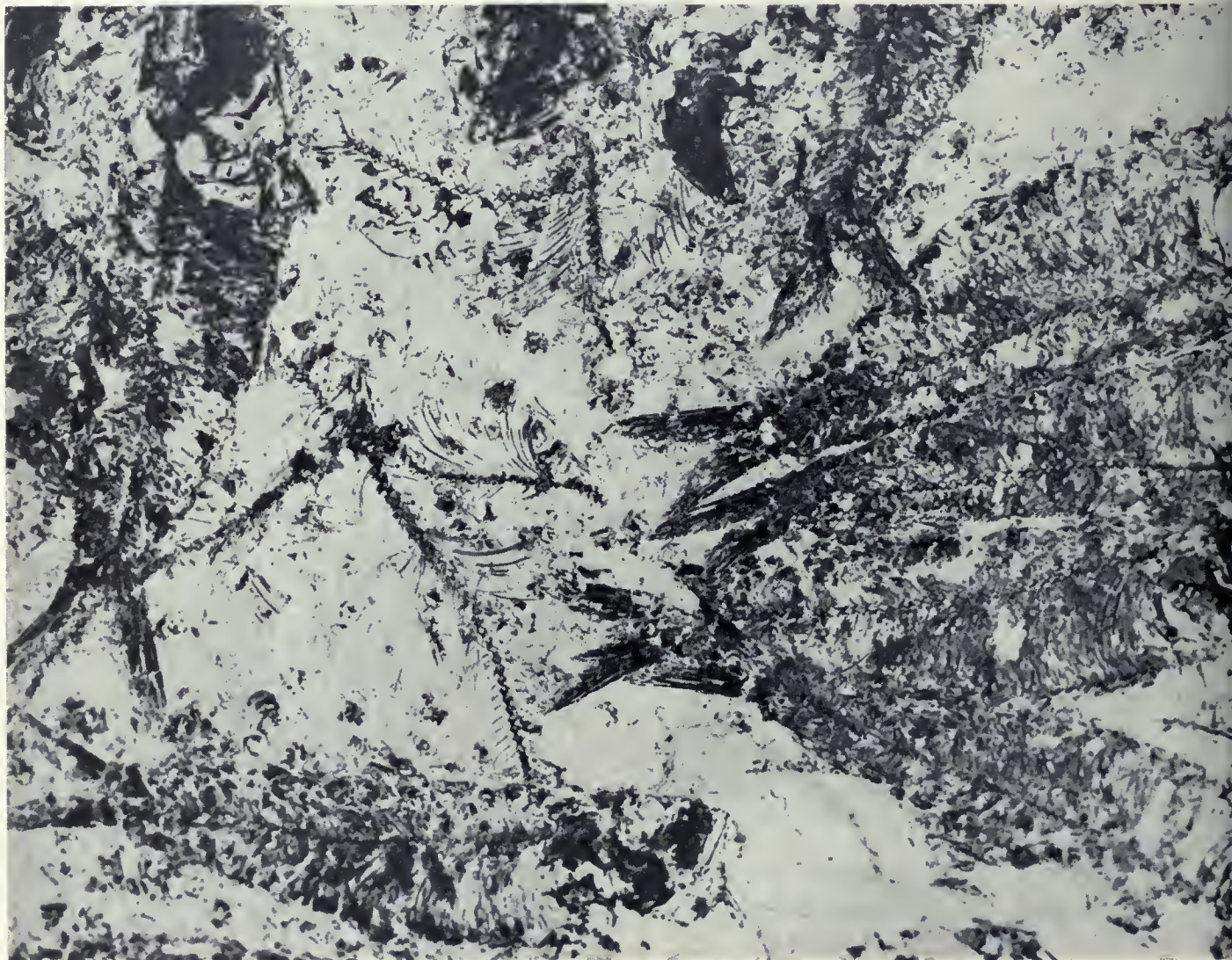


FIGURE 5. Fossil fish (*xyne grex*) in diatomite. Found at Johns-Manville quarry at Lompoc in 1936. About 2/5 natural size. Photo by Mary Hill.





FIGURE 6. Stripping and quarrying operations in one of the Johns-Manville quarries at Lompoc.  
*Photo by Joe Ames, courtesy Johns-Manville.*

sion of Great Lakes Carbon Corporation near Lompoc, Dicalite at WALTERIA, and a small deposit owned by the Basalt Rock Company, Inc., in Napa County were being worked in the state.

The operation south of Lompoc Valley in the northern foothills of the Santa Ynez Mountains, Santa Barbara County, is the largest diatomite operation in the world. It was first worked in 1893 and for many years has been controlled by Johns-Manville. The commercial deposit consists of a 700-foot thickness of pure, thinly stratified diatomite which belongs to the lower part of the Sisquoc formation and covers an area of about 4 square miles. The diatomite here has been preserved in broad synclines, complicated by several minor folds. The diatomite beds range in attitude from horizontal to moderately dipping (maximum  $50^\circ$ ). The best-grade diatomite is thinly stratified, with laminae averaging about  $\frac{1}{32}$ -inch in thickness. It is cream-colored below the surface and dries to a pure white. As quarried, it contains 35 to 50 percent water; however, it holds 75 percent at saturation. The pure air-dried diatomite has a density of approximately 0.5.

#### MINING AND PROCESSING

An account of the Johns-Manville operation at Lompoc has recently been given by Hutt (1949). Mining was largely underground in the early history of operations at Lompoc but is now carried on entirely by open pits in two synclines and an anticline between

them. The diatomite is removed by carryalls and electric-powered shovels. The mining is selective and follows high-quality strata. The diatomite is loaded in 28-yard and 22 $\frac{1}{2}$ -yard bottom dump trucks and is dumped into glory holes situated at convenient points. From the bottom of the glory holes it is hauled in trains to an underground blending and crushing plant. The total length of tunnels is now nearly 3 miles. Tunnels are up to 12 feet in diameter and are driven entirely in diatomite. The glory holes and tunnels are dry, no blasting is necessary, and the material holds up so well that very little ground support is needed. Loaded trains pass through the branch haulage tunnels into the main tunnel and to crude ore bins above the primary blending and crushing plant.



FIGURE 7. An elevating loader loading overburden into a bottom-dump truck in one of the Johns-Manville diatomite quarries.  
*Photo by Joe Ames, courtesy Johns-Manville.*





FIGURE 8. Haulage train transporting crude diatomite from quarry to processing plant, Johns-Manville Products Corporation, Lompoc. Photo by Joe Ames, courtesy Johns-Manville.

The crude is taken to the hammer mills and is distributed by conveyor belts to drying, milling, classifying, and processing units used in the surface plant. Very accurate control of plant feed is maintained. The crude crushed diatomite goes through a series of drying, milling, and classification processes (fig. 10) (Huttl, 1949). The final products include both calcined and uncalcined diatomite but the greater proportion now is calcined.

Johns-Manville formerly operated a quarry for the recovery of natural insulating brick. This operation has been discontinued and a new dry-pressed and calcined fabricated brick is produced instead. It is used for insulating refractories up to 2200° F. During 1956 the company is completing construction of a new plant at Lompoc for manufacture of synthetic silicates (fig. 9). They are to be made directly from crude diatomite by reactions with lime or magnesia under pressure. Resulting will be a new line of products for use as inert absorbents, bulking agents or extenders in paints, paper, cleansers, insecticides, fertilizers and others (Briggs, 1956).

The deposit that has been developed by Dicalite 7 miles southeast of Lompoc is also in the lower part of the Sisquoc formation and is exposed over 1500 acres. Structurally, the deposit lies in a local basin 2 miles long, which includes three synclines and two anticlines striking generally N. 85° W.; dips range from horizontal to 50°.

The major syncline on the Dicalite property is complicated by numerous folds. Some are closed, which makes it possible to quarry selected strata continuously around a trough-shaped synclinal basin. The dips of strata range from nearly flat to 35°.

Land holdings by Dicalite include approximately 750 acres. Operations at this quarry were started in 1948 and originally supplied part of the crude diatomite processed at Walteria in Los Angeles County. Mining is done by carryalls that scrape the diatomite into a 25-cubic yard bin. From the quarries it is delivered to a new processing plant about 7 miles from the mine; some diatomite is still trucked to the Walteria plant. The Lompoc plant was completed in 1952; description of this plant was recently published by Hull, et al., in 1953 (fig. 11). All of the diatomite formerly was trucked to the Walteria plant.

The diatomaceous beds mined by Dicalite on the north side of the Palos Verdes Hills in Los Angeles County have been folded to form a series of minor anticlines and synclines and are faulted along the north side of the deposit. In this area Dicalite leases 308 acres and operates a large quarry and processing plant. Gay and Hoffman (1954) recently gave an account of this operation. Here locally contorted but generally northeast-dipping strata 20-35° are selectively mined and processed at a plant nearby, built by Dicalite in 1930 and purchased by the Great Lakes Carbon Corporation in



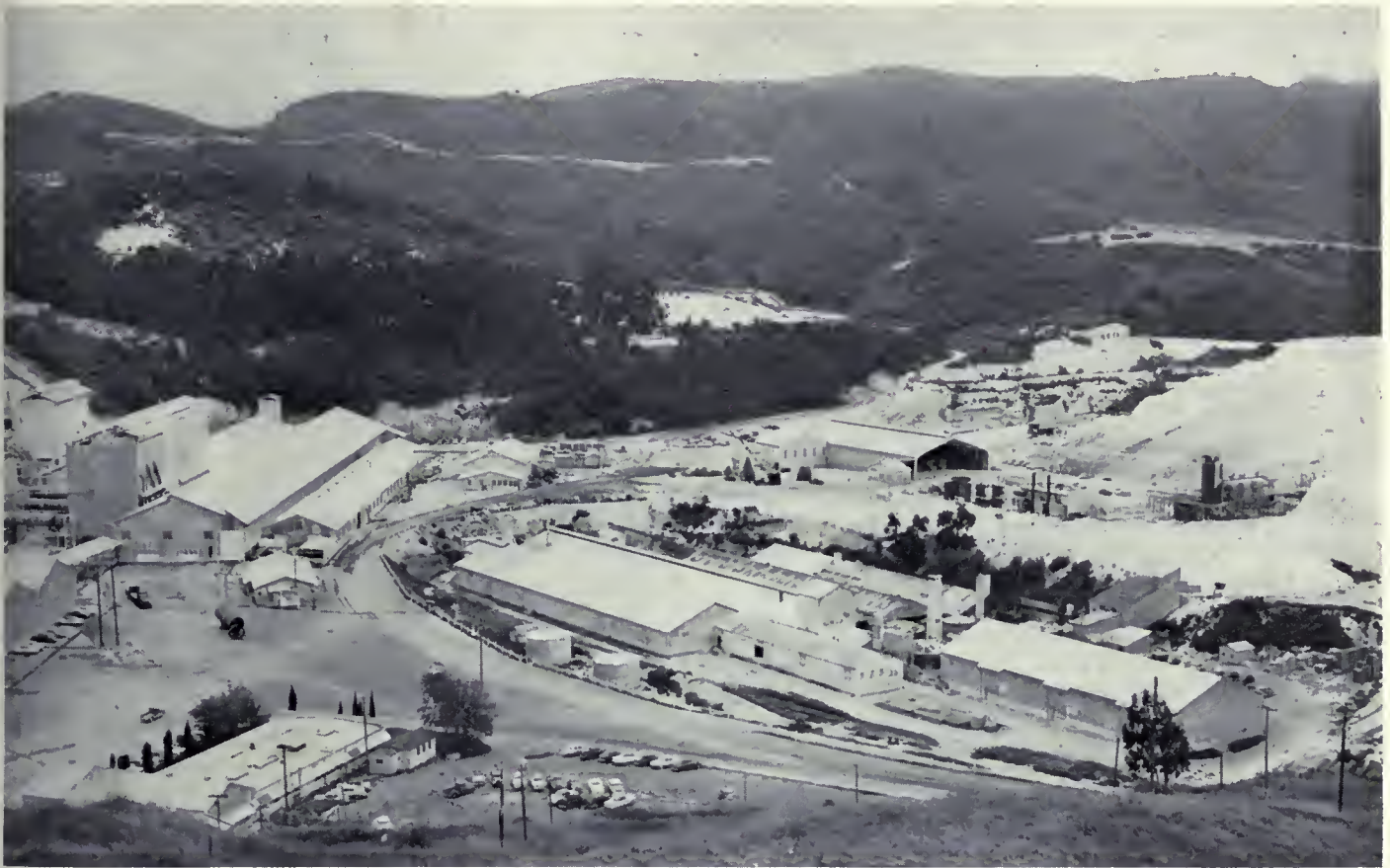


FIGURE 9. Johns-Manville "Celite" plant at Lompoc. The new synthetic silicate plant under construction in 1956 is shown in upper right. Photo by Joe Ames, courtesy Johns-Manville.

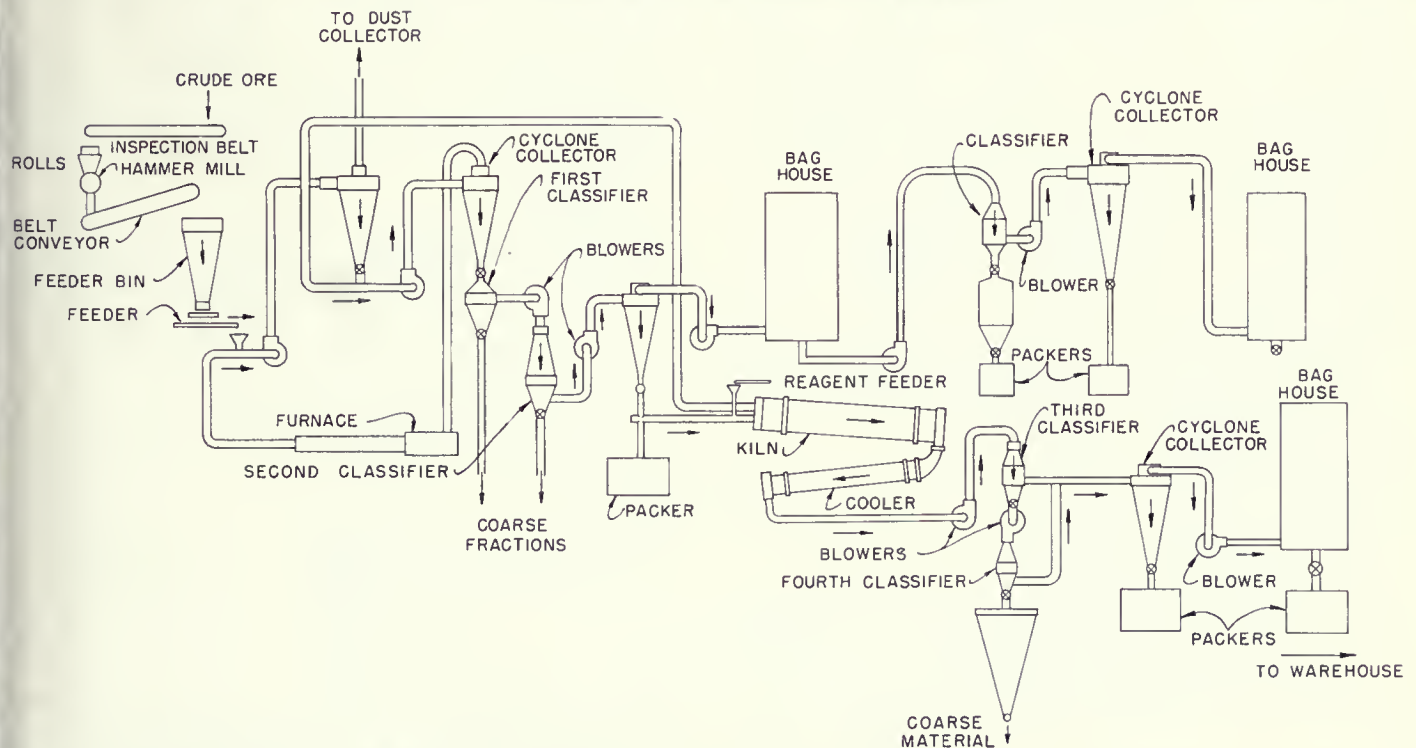


FIGURE 10. Essential steps in processing crude diatomite at Lompoc plant of Johns-Manville (Huttl, 1949). Reproduced by permission of Engineering and Mining Journal. Copyright McGraw-Hill Publishing Company.



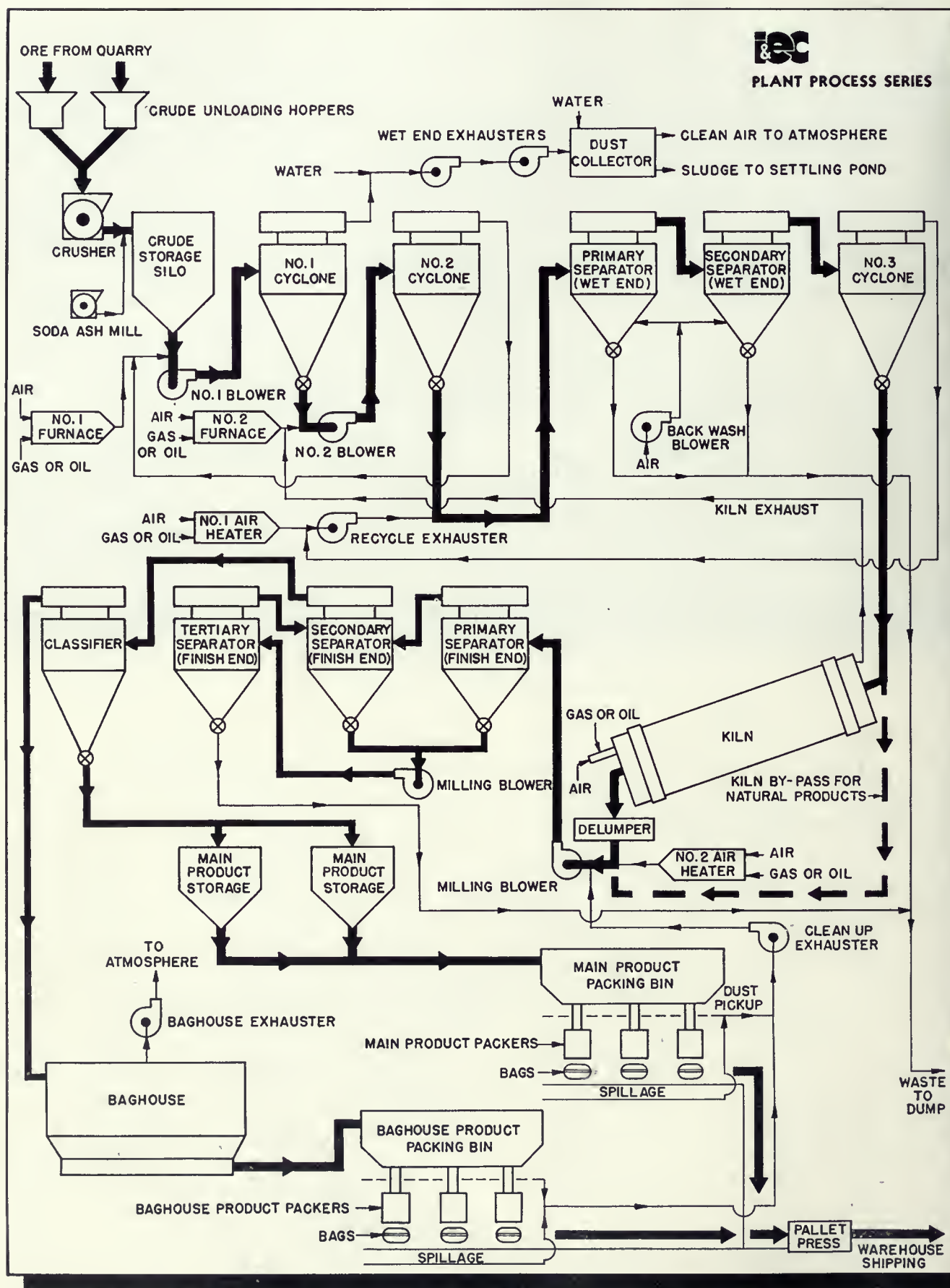


FIGURE 11. Flow sheet for processing of diatomaceous earth at Great Lakes Carbon Corporation, Lompoc. Reprinted from *Industrial and Engineering Chemistry*, vol. 45, p. 256. Copyright 1953 by American Chemical Society.



1944. Although some underground mining was carried on in this area many years ago, Dicalite Division leased the deposit and all of the later operations by Dicalite have been by open pit methods, and, like other diatomite operations, are carried on without explosives. Mining is done very selectively with a man and hand shovel assisting the power shovel in the separation of desirable crude from non-commercial material. Some crude diatomite is left in storage piles to dry before being trucked a short distance to the mill.

After delivery to the mill the crude diatomite is crushed in a hammer mill to about 1 inch size and then dried at 800-900° F. Most goes through a series of processes including calcination in large gas-fired rotary kilns at temperatures of 1600° to 2000° F. Three types of diatomite products result: natural, which has been dried, milled, and air-classified; calcined, which has been dried, milled, burned at a high temperature and air-classified; and processed calcined, which has been dried, milled, subjected to high-temperature fluxing and air-classified.

In early 1954, Dicalite succeeded in greatly expanding its usable reserves of high-grade diatomite in this area by acquiring control of some 6800 acres of land in the Palos Verdes Hills. This includes the 165 acres underlain by high-quality diatomite located 3 miles from the processing plant at Waleria. The surrounding area is one of rapid high-class residential development; therefore a new type of operation is being used to minimize dust, noise, and undesirable appearance. It is a trenching method which includes extraction of the diatomite and refilling of the trench behind the operation. The crude diatomite is trucked from the quarry to the Dicalite plant at Waleria. This operation is expected to make possible a continuing source of supply for the Waleria plant for many years to come.

A deposit of diatomite near Bradley in southern Monterey County was acquired a few years ago by the Dicalite Division of the Great Lakes Carbon Corporation. This diatomite is in the upper part of the Monterey formation and is underlain by porcelaneous rock and cherts.

#### UTILIZATION

The uses of diatomite have been increasing steadily in the past few years in response to very active research and sales efforts by the largest producers. The principal uses in the United States were grouped as follows in 1954 (U. S. Bureau of Mines, 1956): (1) filtration, 51 percent; (2) fillers, 29 percent; (3) insulation, 8 percent; and (4) lightweight aggregate, pozzolanic concrete, abrasives, and miscellaneous, 12 percent. Comparable figures for sales of prepared diatomite in California for the period 1953-55 are, respectively, 62, 25, 8, and 5 percent.

The greatest expansion in the use of diatomite in the past few years has come through its applications in industrial filtration. Sugar solutions were among the first filtered by diatomite but other products now include petroleum, chemicals, varnishes and shellacs, waxes and resins, metallurgical plating solutions, vegetable oils, animal fats, gelatins, antibiotics, and polluted water. The filteraid manufacturing process has become very complex. Nine basic grades of filteraids are produced by Dicalite alone, with the fastest flow rate 20 times

the slowest. The faster grades have lower clarification but the selection of the most suitable grade for a given industrial problem is a matter requiring laboratory filtration tests followed by actual plant usage. In filter use, diatomite powders are mixed with the liquid to be filtered and as the liquid goes through the filter, the diatomite collects to form a porous cake on the filter membrane. The amount of diatomite necessary in a filteraid is usually from  $\frac{1}{10}$  to  $\frac{1}{2}$  of 1% of the weight of the liquid. The low bulk density of diatomite powders (6 to 12 pounds per cubic foot), void volume of 75 to 85 percent, the particle size range of the many species of diatom usually present, and chemical inertness of the material account for much of its value as a filtration medium. Processing of the crude diatomite to produce the filteraid products is highly specialized and industry specifications are rigid.

Diatomite is used as a mineral filler in many products which require bulk and improved toughness, elasticity, absorptiveness, and heat conductivity. Paper products, paints and lacquers, plastics, asphalt products, and insecticides are important products in which diatomite is used.

The high percentage of voids and high melting point (about 2900° F.) of diatomite make it useful in heat and sound insulation. It is used in building construction, in kilns, and in industrial furnaces. Some of the insulating brick manufactured may be used at temperatures as high as 2500° F.

Diatomite has a large number of miscellaneous uses; according to Leppa (1953) over 300 are recognized. Among the more important of these minor uses are in lightweight aggregates and in pozzolanic concrete. Its ability to absorb liquid 150 to 200 percent of its weight without changing form is one of its most useful properties. In California, Airox Company, Casmalia, and

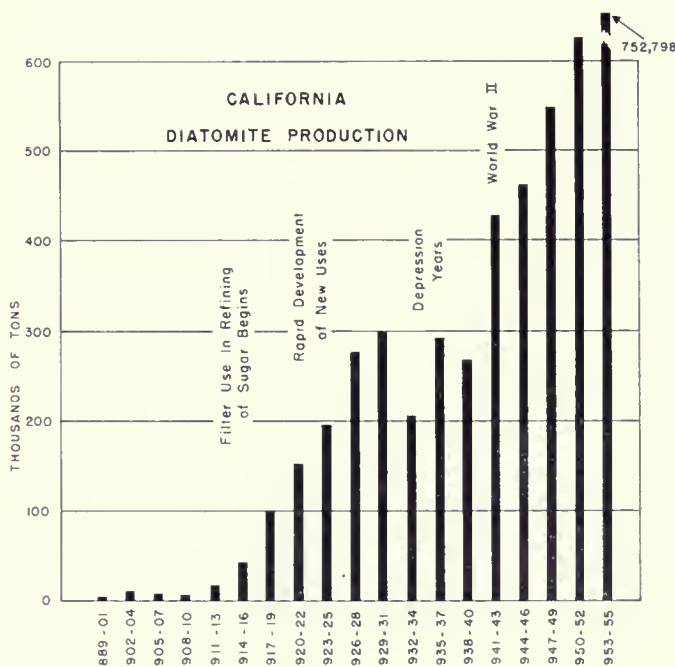


FIGURE 12.



Basalt Rock Company, Napa, have produced diatomite for pozzolan; the Simon Newman Company has produced a diatomite sweeping compound. Diatomite has long been used as a mild abrasive in metal polishes. It is used as a carrier for catalysts in chemical processes and in insecticides, to furnish the necessary silica in ceramic bodies and glazes, as an anti-caking agent in ammonium nitrate fertilizers, in oil-well cementing, and for many other purposes.

#### MARKETING

California, as the leading diatomite-producing state, is followed in order by Nevada, Oregon, Washington, Arizona and New Mexico. Increasing amounts of diatomite are moving out of California to other states and to foreign markets. Although not accurately known, about 75 percent of western output is believed to be sold east of the Mississippi River, and 12 to 15 percent exported. The United States Bureau of Mines (Chandler, 1955) reported that the production of diatomite in 1954 in the United States exceeded 300,000 tons, with a value at the mine of more than \$10,000,000. Average value per ton at the mine, reported to the Bureau of Mines, increased from \$15 in the 1930's to \$30 for the period 1951-1953. The average value per ton of sales of prepared diatomite by California operators for the period 1953-55 rose to \$37.60. California prices have been consistent with these figures, except for a considerably lower price for the small amount of diatomite used for pozzolan in concrete and for much higher prices for a small percentage of special grades sold in bags. The Oil, Paint and Drug Reporter, in 1953, quoted the following prices for processed diatomite: Domestic bags, c.l., ton, Atlantic Coast, \$52-55; California, \$42-45; l.c.l., warehouse, \$85-90.

The outlook for the owner or lessor of a small diatomite deposit in California is not encouraging. In past years small operators producing diatomite for filter aids, floor sweepings, and fillers have had no continued success. Buyers of diatomite products now demand guaranteed volume, require the meeting of rigid and uniform specifications, and expect engineering advice and consultation. The successful seller must therefore control

very large deposits of high quality material, must operate an expensive processing plant, and must carry on continuing research in the development and marketing of diatomaceous products. Present operators in California have reserves of diatomite sufficient for many years of operation and need not purchase crude diatomite from other sources. However, the possibility of discovery and development of large new deposits still exists in California and the future may bring into use known deposits which are not now considered of commercial quality. Rapidly expanding markets, the development of new diatomite products and uses, and satisfactory reserves of raw materials forecast increasing over-all production of diatomite in California in the next few years.

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*Production of diatomite in California, 1889-1955 \**

Year	Tons	Value	Year	Tons	Value
1889-----	39	\$1,335	1914-----	12,840	\$80,350
1890-92-----	0	0	1915-----	12,400	62,000
1893-----	50	2,000	1916-----	15,332	86,649
1894-----	51	2,040	1917-----	24,301	127,510
1895-96-----	0	0	1918-----	35,963	189,459
1897-----	5	200	1919-----	40,200	217,800
1898-1901-----	0	0	1920-----	60,764	1,056,260
1902-----	422	2,532	1921-22-----	90,739	1,016,675
1903-----	2,703	16,015	1923-25-----	193,064	5,729,736
1904-----	6,950	112,282	1926-28-----	275,403	1,995,923
1905-----	3,000	15,000	1929-31-----	300,017	4,848,661
1906-----	2,430	14,400	1932-34-----	203,228	3,104,154
1907-----	2,531	28,948	1935-37-----	290,908	4,243,572
1908-----	2,950	32,012	1938-40-----	266,358	3,941,941
1909-----	500	3,500	1941-43-----	425,745	6,692,051
1910-----	1,843	17,617	1944-46-----	460,654	9,324,111
1911-----	2,194	19,670	1947-49-----	546,144	14,249,445
1912-----	4,129	17,074	1950-52-----	626,288	18,801,913
1913-----	8,645	35,968	1953-55-----	752,798	28,299,664

\* From 1923 to date, 3-year combinations are used to conceal annual output of individual operators.



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## FELDSPAR

BY LAUREN A. WRIGHT

Feldspar, which is used mainly as a ceramic material, has been mined from pegmatite dikes in California since the early 1900's. Since 1952, it also has been recovered by the flotation of beach sand in Monterey County. Through 1955, the pegmatite operations had yielded a total of about 170,000 tons of potash feldspar, and the beach sand plant already had produced several tens of thousands of tons of soda-potash feldspar.

Since 1942, when the largest of the pegmatite feldspar mines in California was shut down, all but a small part of the potash feldspar used in California has been quarried near Kingman, Arizona. Although pegmatite feldspar deposits are numerous in southern California, limited demand and high mining costs generally have made their operation unprofitable.

*Mineralogy and Sources.* The minerals of the feldspar group are essentially silicates of aluminum in combination with various proportions of potassium, sodium and calcium. The principal feldspar species are orthoclase and microcline (both  $\text{KAlSi}_3\text{O}_8$ ), albite ( $\text{NaAlSi}_3\text{O}_8$ ) and anorthite ( $\text{CaAl}_2\text{Si}_2\text{O}_8$ ). These ideal compositions, however, are rare in nature. Orthoclase and microcline ordinarily contain appreciable proportions of soda. Albite and anorthite are end members of a continuous series known as plagioclase, a feldspar in which small proportions of potash generally exist. Microcline and orthoclase commonly contain subordinate albite to form irregular intergrowths of potash and soda feldspar. Such intergrowths, known as perthite, constitute most of the feldspar of commerce.

As used commercially, the term "feldspar" includes material that ranges from the pure mineral to feldspar-quartz mixtures containing as much as 25 percent quartz. "Potash-spar" and "soda-spar" are common designations based on the relative abundance of the two elements.

Feldspar is the most abundant constituent of igneous rocks and is common in many metamorphic rocks and in detrital sedimentary rocks. Most of the feldspar, however, is mixed with other minerals, principally quartz, mica, and ferromagnesian minerals, and occurs in grains that are too small to recover without beneficiation. For many years, before the development of froth flotation methods to recover feldspar, high-quality feldspar was obtained only from coarse-grained concentrations of the mineral in certain pegmatite bodies.

Mineable concentrations of pegmatite feldspar ordinarily lie in the central parts (intermediate zones and cores) of complex dikes, and form lenses and pods from a few feet to several hundred feet in maximum dimension. Much coarse-grained pegmatite consists of feldspar-quartz mixtures, and individual crystals several feet in diameter are not uncommon. In many pegmatite bodies, coarse perthite crystals contain regularly arranged inclusions of quartz to form an intergrowth known as graphic granite.

In general, only pegmatite composed largely of potash feldspar crystals at least 6 inches in maximum dimension has been considered to be mineable for feldspar. In some deposits the perthite crystals or crystal aggre-

gates are large enough to permit the large-scale breaking of nearly pure masses of feldspar, but in most deposits the coarse crystals of perthite and quartz are so intimately mixed that they must be broken together and then hand sorted. Other less abundant minerals, such as mica and garnet, also must be carefully removed from the feldspar concentrates.

With the advent of flotation methods for the beneficiation of feldspar-bearing rocks, a less selective mining of pegmatites and other granitic rocks, as well as feldspathic sands, became possible. The treatment of these materials, however, generally yields potash feldspar and soda-lime feldspar mixtures that are markedly lower in potash than the feldspar that has been specified for most ceramic uses. Consequently, selectively mined, coarse-grained pegmatite continues to be the major source of high-quality potash feldspar. Pegmatite bodies also contribute much of the material for beneficiation, but the principal sources are finer-grained rocks that can be broadly classified as leucogranites.

In a general way, feldspar enters into the mineral industry as a component of sand, gravel, and stone (see corresponding sections in this volume). Feldspar also is the principal constituent of nepheline syenite and aplite—two rocks which are competitive with feldspar in certain ceramic uses.

Since the early 1920's pegmatite bodies in North Carolina have been the principal source of feldspar in the United States and in 1953 contributed about two-thirds of the nation's 453,000-ton output. The remainder was mined mostly from deposits in Colorado, Maine, New Hampshire and South Dakota.

Much of the high-potash feldspar consumed in California, and virtually all of such material brought into the state, has been obtained from pegmatite dikes near Kingman, Arizona, that are operated by the Consolidated Feldspar Department of the International Minerals and Chemicals Corporation. By 1955, the Kingman locality had yielded about 150,000 tons of feldspar which had been marketed largely in California. At this locality, several pegmatite dikes \* cut schistose country rock. The larger dikes are about 90 feet in maximum width and several hundred feet long, and contain interior zones of very coarse-grained quartz-perthite pegmatite that conform with bulges in the walls of the dikes. These bodies, in which large reserves of feldspar remain, have been mined in four quarries all within an area about 1,500 feet square. The feldspar is hand sorted and trucked to a mill at Kingman.

*Localities in California.* Pegmatite bodies associated with the Mesozoic igneous rocks of the Southern California batholith in Riverside and San Diego Counties have been the source of most of the ceramic-grade, potash-feldspar produced in California. Feldspar of this type also has been mined from pegmatites in the western foothills of the Sierra Nevada, in Monterey County, and at scattered localities in the desert regions of eastern and southern California (fig. 1). In only a

\* Data on the Kingman pegmatites has been kindly supplied by R. H. Jahns of the Division of the Geological Sciences, California Institute of Technology.



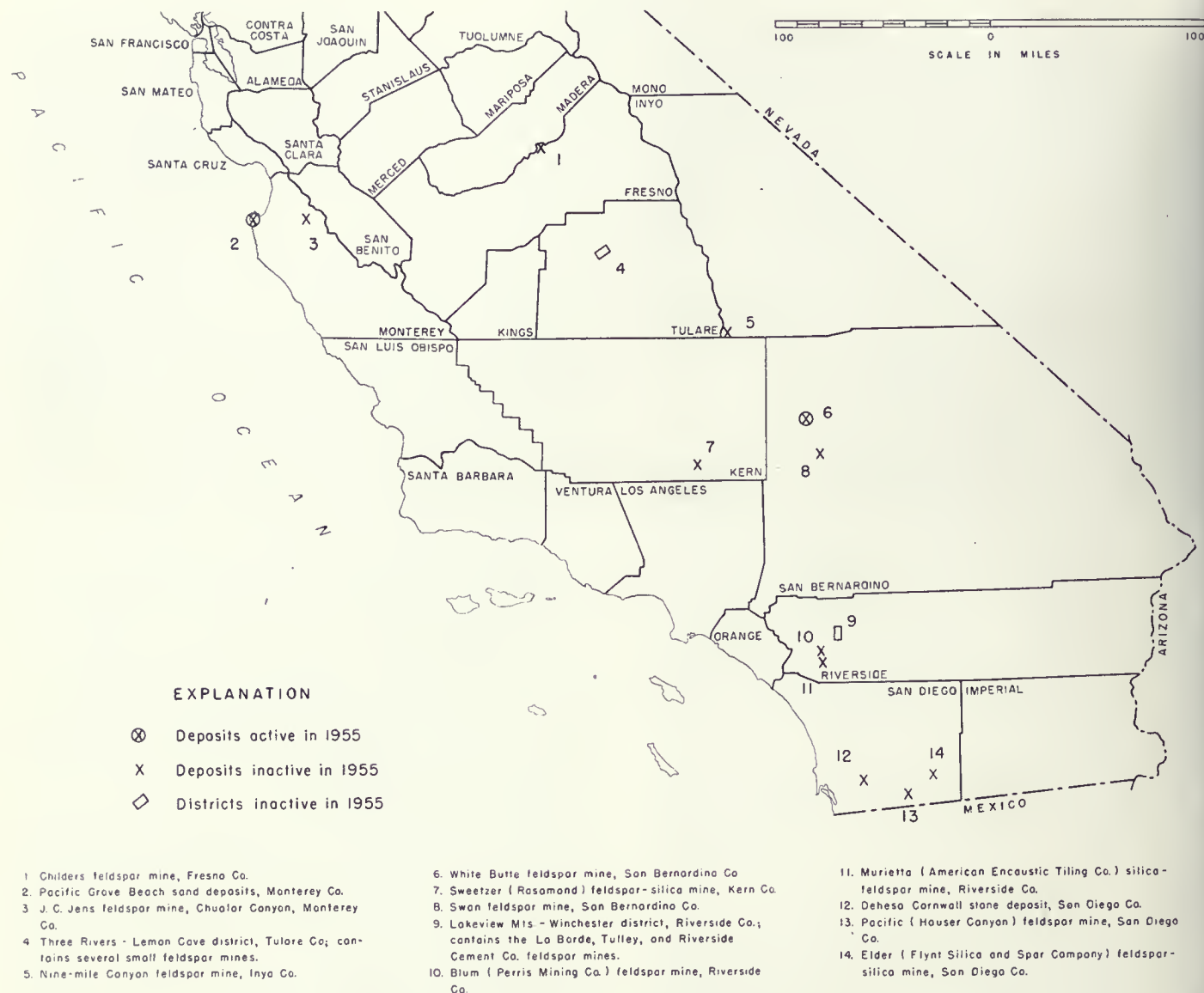


FIGURE 1. Index map of southern California, showing locations of the principal sources of feldspar in California.

small proportion of the total number of pegmatites in California is the potash feldspar in large, easily mined concentrations and, of these, only the more accessible have been developed. In all, about 50 pegmatite feldspar properties in California are known to have been productive, and the combined output of these is about 170,000 tons.

The Pacific mine, about 5 miles north of Campo in San Diego County, yielded about 87,000 tons of feldspar during its active period which extended from about 1921 to 1942. This output is by far the largest, and the operating period the longest of the potash feldspar mines of California. Most of the mining was done by the Standard Sanitary Manufacturing Company.

The Pacific pegmatite (figs. 2 and 3; Foote, 1951) forms a 45° dip-slope on the north side of Houser Canyon; it is a lenticular body about 500 feet in exposed length extends down-dip for at least as far, and is about

80 feet in maximum exposed width. It contains a border zone, about 5 feet thick, composed mostly of graphic granite; a wall zone, 5 feet to 20 feet thick, of coarse-grained, quartz-perthite pegmatite; an intermediate zone, 5 feet to 30 feet thick, of blocky perthite; and a quartz core. The body is bordered by granitic and metamorphic rocks and contains elongate inclusions of schist.

Feldspar has been mined, from both the wall zone and intermediate zone, by benches in an open cut which is about 220 feet high, and 50 to 200 feet wide. When the property was shut down, most of the feldspar that could be mined by surface methods had been removed. The mined material was crushed, screened, hand-sorted to two grades and trucked to a mill at Campo (Sampson, and Tucker, 1931, pp. 430-431). The Elder feldspar mine, also near Campo, was worked intermittently during a ten-year period ending in 1929, but its total recorded yield was only about 5,200 tons.





FIGURE 2. Photo of Pacific feldspar mine, Houser Canyon, San Diego County. Feldspar-bearing pegmatite forms dip-slope of canyon wall. This mine was active from 1921 to 1942 and has been the principal source of potash feldspar in California. Photo by R. H. Jahns.

A pegmatite about 3 miles north of Murrieta, Riverside County was worked during the period 1919-1930 by the American Encaustic Tiling Company, and has since lain idle. Silica was the principal product, but several thousand tons of potash feldspar also were mined. Potash feldspar has been produced commercially from about 30 other properties in San Diego and Riverside Counties. But all were short-lived and less productive than the Pacific, Elder and Murrieta operations. Several, however, had single-year outputs that exceeded 1,000 tons. These include the Riverside Portland Cement Company, Tully, and La Borde deposits near Lakeview, the Blom (Perris Mining Company) deposit near Perris, and the Machado deposit 3 miles north of Winchester.

Second to the Pacific mine in total recorded production of potash feldspar is the White Butte mine, which underlies a low hill about 18 miles southeast of Atolia, San Bernardino County. The White Butte deposit was opened in 1940, had yielded about 18,000 tons through 1955, and has been worked entirely as a captive operation by Gladding, McBean and Company (Wright, et al., 1953, pp. 163-165). It is a pod-like body about 300 feet by 200 feet in exposed dimensions composed mostly of exceedingly coarse-grained perthite-quartz pegmatite. The feldspar has been quarried selectively and the quartz remains as pillars in the otherwise flat quarry floor.

Much of the early interest in feldspar mining in California centered about a group of pegmatite dikes near Three Rivers and Lemon Cove, Tulare County. The combined output of these deposits, however, did not exceed 8,000 tons, and was confined to the period 1911-20. During this period also, the J. C. Jens mine, about 5 miles east of Chualar in Monterey County, was active and yielded about 5,500 tons of potash feldspar.

Feldspar deposits from which outputs of 1,000 to 5,000 tons have been obtained exist at other widely scattered localities (Tucker and Sampson, 1931), and include the Sloan deposit,  $3\frac{1}{2}$  miles north of Hinkley, which was worked intermittently during the period 1916-20; the

Sweetzer (Rosamond) deposit, 3 miles northwest of Rosamond, Kern County, which was most active from 1925 to 1932; the Nine-mile Canyon deposit, about 5 miles west of Linnie, Inyo County, which was worked from 1928 to 1932; and the Childers deposit (Logan, Braun, and Vernon, 1951, p. 502), 4 miles northwest of Auberry, Fresno County, worked mainly from 1937 through 1944.

An aplitic dike-rock composed mostly of potash feldspar that resembles the "Cornwall stone" mined near Cornwall, England, has been quarried in the Dehesa area of San Diego County (Tucker, 1925, p. 358). The deposit was worked in the 1920's and early 1930's. Its output, which probably totaled several thousand tons, was used in tile manufacture (Stewart, R. M., personal communication, 1956).

Anorthosite, a rock composed almost wholly of calcic plagioclase, occurs in virtually inexhaustible deposits in the northwestern part of the San Gabriel Mountains (Oakeshott, 1937; Higgs, 1954; also see sections on titanium in this volume). The anorthosite in this area is very coarse grained and consists of about 97 percent andesine, and a remainder composed mostly of disseminated apatite, zircon, chlorite, hornblende, biotite and ilmenite-magnetite. Although quarrying of the anorthosite has been attempted at several places (Sampson and Tucker, 1931), the operators have failed to find a continuing market for it.

In 1952, with the establishment of a flotation unit to treat beach sands at one Pacific Grove plant of Del Monte Properties Company, the production of feldspar in California increased markedly. The beach sands at this locality are exceptionally clean and consist of about 46 percent feldspar divided almost equally between sodic plagioclase and potash feldspar. The flotation of these sands, described in the specialty sand section of this volume, yields a feldspar concentrate which contains about 20 percent  $\text{Al}_2\text{O}_3$ , 5 percent  $\text{Na}_2\text{O}$ ,  $4\frac{1}{2}$  percent  $\text{K}_2\text{O}$ , 21 percent  $\text{CaO}$ , and 0.1  $\text{Fe}_2\text{O}_3$ .



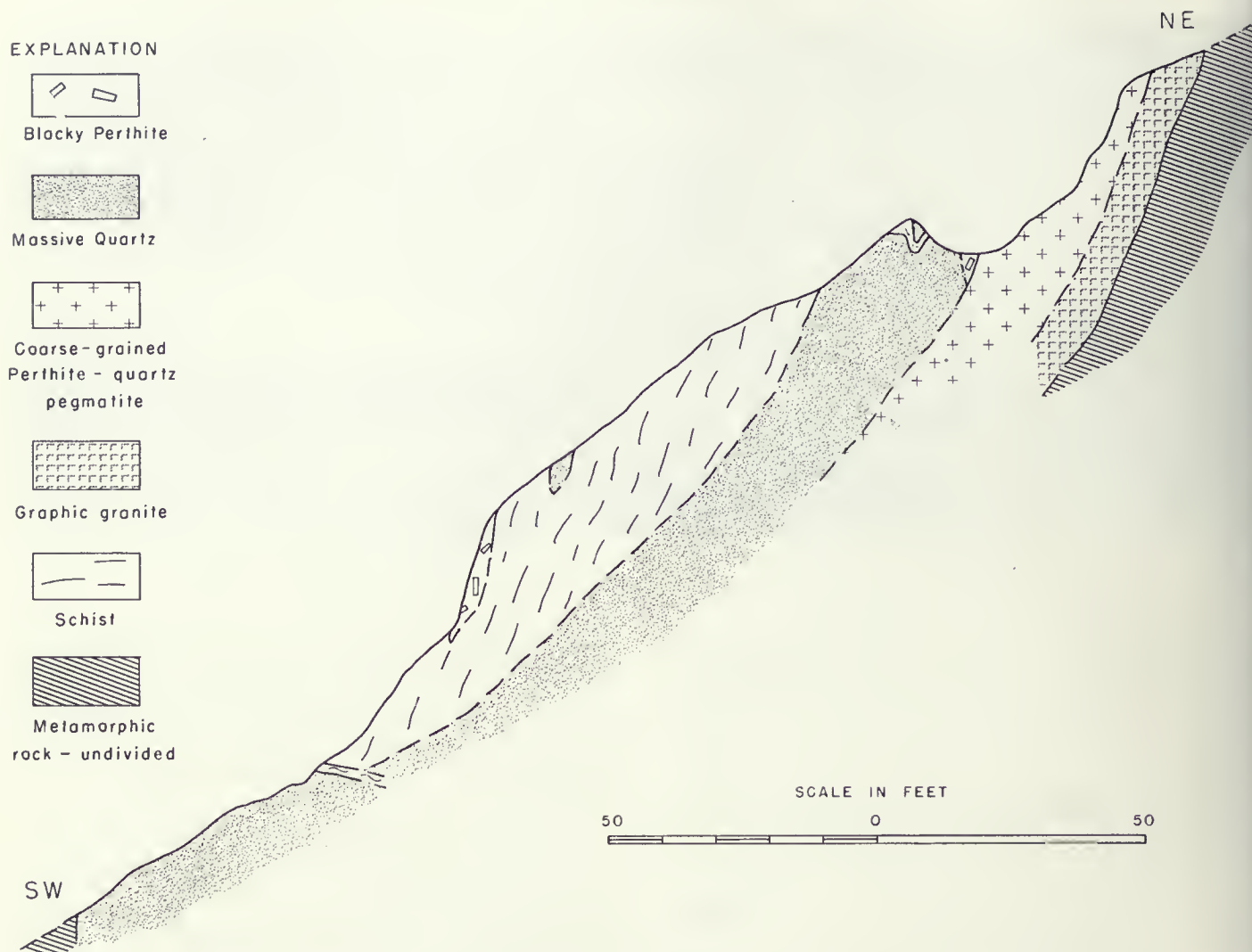


FIGURE 3. Geologic section through pegmatite body at Pacific feldspar mine, San Diego County. (After Foote, 1951.)

**Mining Methods and Treatment.** Most of the feldspar that has been mined in California, as well as elsewhere, has been recovered by surface methods. Although limited underground workings exist at several of the feldspar mines in California, mining costs, the discontinuous nature of the deposits, and the relatively low prices for the mined product, have hindered such operations. The potash feldspar concentrations in coarse-grained pegmatite have been worked mainly by small operations. Even in the more productive districts of the United States few mines have yielded more than 50 tons a day of coarse-grained potash feldspar.

All feldspar operations seek the recovery of material free from impurities, especially iron oxide stains, tourmaline, and mica. Quartz, formerly considered an impurity, is now generally regarded as a diluent that may comprise as much as 25 percent of commercial feldspar. In common practice the feldspar is quarried selectively by conventional drilling and blasting methods, then hand-sorted and, if necessary, hand-cobbed. At some mines the quarry-run material is first coarsely crushed and then hand picked from a sorting belt, as was done

at the Pacific mine in San Diego County. The sorting commonly yields a silica coproduct and by-products of mica, beryl, and other, less common minerals.

The potash feldspar generally is sorted into two grades: No. 1 which is of highest quality and contains no more than a few percent of quartz; and No. 2, which is essentially free of bothersome impurities, but contains a quartz percentage higher than in No. 1 but less than about 25 percent. Some operations yield a No. 3 grade which contains iron stains and/or a quartz fraction greater than 25 percent, and which is barely saleable. The distinctions between the three grades commonly vary from district to district.

A simple and much-used feldspar milling procedure involves: (1) a crushing of the sorted material to  $\frac{1}{2}$  in. or  $\frac{3}{8}$  in.; (2) passage through a rotary drier (from which mica, clay, and fines are removed as waste) commonly followed by passage through a magnetic separator; (3) grinding in silex-lined pebble mills; and (4) passage either to an air separator or to a vibrating screen. Other, more complex, procedures are essentially modifications of this flow sheet and permit the blending



of different mine products, automatic sampling, and a magnetic treatment of the ground product.

Pegmatite and other granitic rocks for flotation feed are mined in larger scale and less expensive operations than those that develop the coarse-grained potash feldspar concentration. Moreover, the froth flotation of feldspar provides a more efficient recovery of the mineral components, an outlet for material formerly discarded as waste in feldspar mines, and a method of recovering feldspar from sand, as is done at Pacific Grove in California.

**Utilization.** Feldspar is useful mainly because, as a constituent of glass, fired clay products, and enamels, it promotes fusion during firing and imparts strength, toughness, and durability to the finished products. In glass batches, feldspar also improves workability and retards devitrification. As feldspar is harder than most ceramic ware and grinds to sharp-edged, flat-faced equant fragments, it is effective as a mild abrasive.

Although in the period from 1935 to 1955 the annual production of feldspar in the United States rose from about 250,000 tons to nearly 500,000 tons, the use pattern has generally been in the range of 50 to 65 percent for glass, 30 to 40 percent for pottery, 3 to 10 percent for enamel, and 1 to 5 percent for other materials including abrasives and dental and electrical porcelains. For many years virtually all of the commercial feldspar consumed in California was used in the manufacture of pottery, whereas the natural sands used by local manufacturers of glass contained sufficient feldspar. With the growth of the glass industry in the state and with its increased use of high-silica sand, the feldspar tonnage consumed in California is believed to have become about equally divided between the glass and pottery manufacturers.

Rigid feldspar specifications, covering fineness of grinding, chemical classification, and chemical analysis, have been recommended by the National Bureau of Standards (1930), but less stringent standards are met in practice. For glass manufacture high-alkali feldspar is specified, as the contained potash or soda supplant equal amounts of soda that otherwise would be supplied by the soda ash fraction. Mixtures of potash and soda feldspar, like those obtained by the flotation of ground pegmatite and aplite or by the flotation of the beach sands at Pacific Grove, are now in general use by the glass industry. Glass feldspar comprises  $\frac{1}{20}$  to  $\frac{1}{5}$  of individual batches, should contain no more than 0.10 of iron oxide, and should be ground to minus 20 mesh with little or no dust.

For enamel and most pottery a high-potash feldspar still is required, as it provides a wider firing range and greater resistance to devitrification than other feldspars. Pottery and enamel feldspar also should contain less than 0.10 percent iron oxide, should fire white or nearly so and should be consistently of uniform composition. Pottery feldspar ordinarily is ground to minus 200 mesh and enamel feldspar to minus 140 mesh.

**Marketing and Prices.** The market for feldspar in California has been smaller, in proportion to population, than in the eastern United States mainly for these reasons: (1) much of the pottery marketed in California is manufactured in the East, (2) most of the glass sand that has been mined in California is feldspathic and requires little or no additional feldspar, and (3) one of the principal local uses dwindled when, in the mid-nineteen thirties, tale largely replaced feldspar in wall tile manufacture.

An increased market for feldspar in California, however, has developed with the growth of a local glass industry and the expansion of pottery production in California. In the mid-1905's, the feldspar consumed annually by these two industries lay in the general range of 25,000 to 35,000 tons.

The renewal of potash feldspar mining in California, to supply the pottery market, is hindered by several factors. Feldspar is a relatively low-cost commodity that must be mined, sorted, and milled with much care, yet inexpensively. To develop and retain a feldspar market a producer must be able to provide a uniform product over a period of years. Moreover, little or no market exists for the crude material, so that he must provide for grinding either at his own or someone else's mill.

In other areas of the United States, owners of small feldspar mines have successfully worked them by selling crude feldspar to operators of centrally located pebble mills. Such outlets for feldspar do not exist in California.

Although the market for soda feldspar in the glass industry apparently will continue to increase, the recovery of soda feldspar, by means of quarrying and beneficiation of granitic rock, probably will not be attempted as long as the Pacific Grove beach sands or other sand deposits of similar composition remain available in California.

In the mid-1950's soda feldspar concentrates unbagged were valued in the ranges of \$7 to \$10 unground, and \$17 to \$20 ground to minus 325, f. o. b. Pacific Grove. In 1956, the potash feldspar mined at Kingman, Arizona,

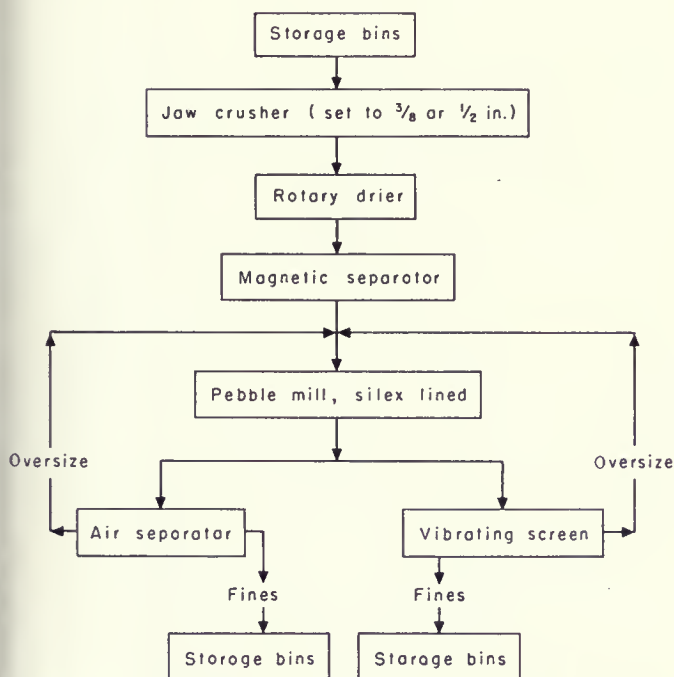


FIGURE 4. Generalized flow sheet of typical feldspar mill.



was being sold, ground to 200-mesh and in carload or truckload lots, at \$20.75 per ton f. o. b. Kingman.

Smaller lots of Kingman feldspar were available through jobbers in the Los Angeles and San Francisco areas. In 1956, the following freight rates for feldspar were in effect: Kingman to Los Angeles, \$6 per short ton, minimum weight 50 tons, and \$7 per short ton, minimum weight 25 tons; Kingman to San Francisco, \$9.20 per short ton, minimum weight 50 tons, and \$12.40 per short ton, minimum weight 25 tons.

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## FLUORSPAR

By CHARLES W. CHESTERMAN

Fluorspar is an important nonmetallic industrial mineral used principally as a flux in the open-hearth process of steel manufacture. The development of an iron and steel industry in California has increased the consumption of metallurgical and acid-grade fluorspar, but the production of fluorspar in California has been small, intermittent and unable to keep pace with the demands of the steel industry. The total fluorspar production in California to date has been but a few hundred tons; virtually none was mined in 1954. The bulk of acid and metallurgical grades of fluorspar consumed in California is shipped into the state from Nevada. This amounts to 15,000 or more short tons annually.

*Mineralogy and Geological Occurrence.* Fluorspar or fluorite ( $\text{CaF}_2$ ), is the only fluorine-bearing mineral of economic importance. When pure, it contains 48.7 percent fluorine and 51.3 percent calcium. Fluorite has a hardness of 4 in the Mohs' scale, compared with 3 for calcite and 7 for quartz, and a specific gravity of 3.00 to 3.25. It has three perfect cleavages and occurs in a multitude of colors ranging through dark purple, blue, and yellow to white and colorless. Fluorite is easily distinguished from calcite by its lack of effervescence when treated with dilute hydrochloric acid.

Fluorite occurs in a great variety of geological settings—as fissure fillings, as replacement deposits in sedimentary rocks, as fillings of solution cavities near faults, and as residual deposits.

Most of the world's output of fluorspar comes from deposits in Mexico, Spain, Italy, Germany, Canada, and the United States. The bulk of the world's fluorspar is consumed by the producing country, except Mexico and Spain which export virtually all of their production. The fluorspar of commercial interest generally occurs in veins and irregular bodies enclosed in sedimentary, metamorphic, or igneous rocks. They are replacement deposits and cavity fillings, and have a fluorspar content ranging from 50 to 95 percent. The largest deposits, including those in the United States and Mexico, contain fluorspar that is measurable in hundreds of thousands of tons.

A large part of the fluorspar consumed in California comes from deposits near Beatty, Nevada where fluorspar is mined from veins 4 to 20 feet thick in brecciated and faulted Paleozoic limestone. Fluorspar shipped into the state from Montana is obtained from lenticular bodies in granite and gneiss from Darby.

*Localities in California.* In California, fluorspar deposits have been noted in Inyo, Kern, Los Angeles, Lake, Mono, Riverside, San Bernardino, San Diego, Santa Clara, Tulare, and Yolo Counties. Deposits that have attracted attention as potential commercial sources of fluorspar exist in the Deep Springs Valley, the Darwin district, and in the Panamint Range, Inyo County; in the White Mountains, Mono County; in the Little Maria, Palen, and Orocopia Mountains, Riverside County; in the Cave Canyon district, in the Providence, Riverside, Shadow, and Sidewinder Mountains; and at Clark Mountain, San Bernardino County.

In Deep Spring Valley, Inyo County, deep-purple fluorspar occurs in veinlets in metamorphosed limestone. The veinlets range from a fraction of an inch to several inches in thickness, and as much as 20 feet in length. The larger veins contain quartz, orthoclase, and muscovite (Knopf, 1912). In the Darwin district, Inyo County, coarsely crystalline fluorite occurs as a gangue mineral in the silver-lead deposits (Knopf, 1913). Although there are local concentrations of the fluorite, it was never recovered commercially from either area.

At a deposit on the north slope of Warm Spring Canyon, Panamint Range, Inyo County, fluorspar occurs in veins from one foot to 10 feet wide that cut Archean granite gneiss (Crosby and Hoffman, 1951, p. 632). The  $\text{CaF}_2$  content of representative samples ranged from 29 to 65 percent.

In Mono County, fluorspar occurs with andalusite, muscovite, damourite, lazulite, corundum, pyrophyllite, and rutile in the Champion Sillimanite Incorporated mine, on the western slope of the White Mountains (Jeffery and Woodhouse, 1931, p. 461). Fluorspar was never recovered commercially from this deposit. Fluorite also occurs in fissures in limestone with coarsely crystalline muscovite in the White Mountains, a few miles north of Westgaard Pass, Inyo County. The veins range from a fraction of an inch to 2 feet in width and have been traced on the surface for several tens of feet. They have been prospected by several shallow pits, but are undeveloped commercially.

At a locality near the north end of the Palen Mountains, eastern Riverside County, green, white, and purple fluorspar occurs as disseminated grains and bunches closely associated with malachite and azurite. A deposit on the east slope of the Little Maria Mountains about 14 miles south of Rice, Riverside County, contains several fluorspar-bearing veins from 18 inches to 3 feet in width, and up to 40 feet in length. These occur in quartzite and mica schist. An analysis representative of 130 tons which was shipped from this deposit in 1944 to the National Supply Company, Torrance, California, showed 87 percent  $\text{CaF}_2$ , 4 percent  $\text{SiO}_2$ , 0.47 percent  $\text{CaO}$ , 2.25 percent  $\text{Al}_2\text{O}_3$ , and 0.15 percent  $\text{Fe}_2\text{O}_3$ .

The largest number of known fluorspar deposits in California is in San Bernardino County. Numerous veins of fluorspar occur in the Cave Canyon district near Afton. Here the fluorspar is associated with fine-grained andesitic rocks which occur as intrusive bodies or flows. The volcanic rocks are fractured, and form breccias which, in places, contain much coarse crystalline fluorspar. The fluorspar-bearing zones of brecciated andesite are irregular and range from one foot to 50 feet in thickness. They are traceable for nearly 2000 feet on the surface. Some of the fluorspar occurs in veins that range from a few inches to 4 feet in thickness. The richer parts of the fluorspar-bearing zones locally contain 10 to 40 percent fluorite, but such areas are small. Both silica and calcite are present, but metallic sulfides are lacking. Analysis of representative samples showed a range of 35 to 86 percent  $\text{CaF}_2$ , 8 to 44 percent  $\text{SiO}_2$ ,



## FLUORSPAR DEPOSITS IN CALIFORNIA

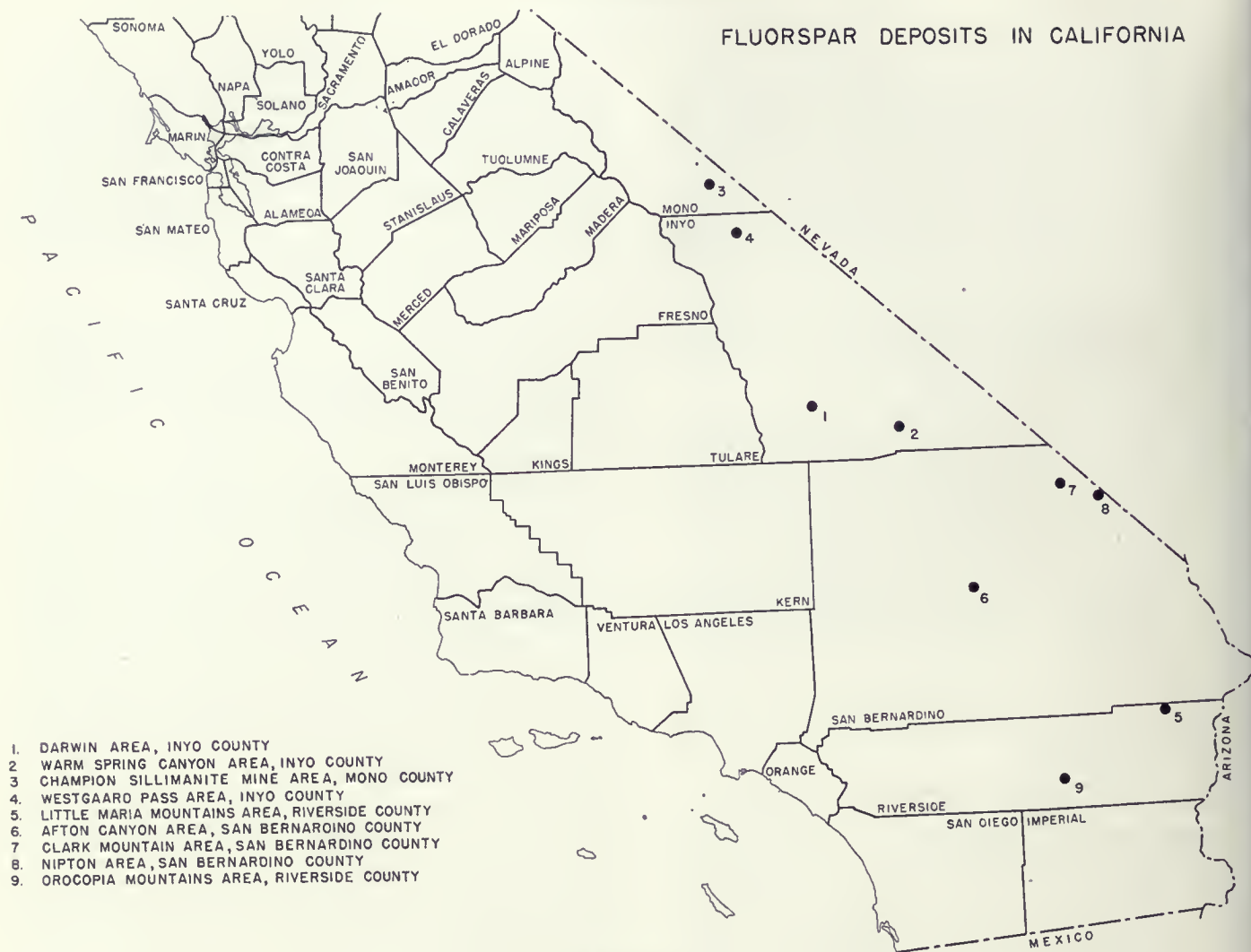


FIGURE 1.

and 2 to 29 percent  $\text{CaCO}_3$  (Burchard, 1933, pp. 373-374).

On the north side of Clark Mountain near Mountain Pass, eastern San Bernardino County, fluorspar occurs with sericite in replacement veins along discontinuous shear zones in the Goodsprings (Cambrian) dolomite. The fluorspar veins range in width from 4 to 50 feet, in length from 100 to 400 feet, and contain on the average between 40 and 60 percent fluorite. They have been prospected through several openings and one inclined shaft 85 feet deep was bottomed in fluorspar (Crosby and Hoffman, 1951).

Another fluorspar deposit lies a few miles east of Nipton, near the California-Nevada boundary line. The fluorspar occurs in pre-Cambrian gneiss and forms veins from 12 inches to 3 feet wide. The vein material is low grade and most of it would require concentration to bring it up to a marketable product. One narrow vein, however, yielded material containing 85 percent fluorite (Burchard, 1933, p. 395).

Other deposits of fluorspar in San Bernardino County include occurrences at the following localities: the southern part of the Riverside Mountains, 26 miles

south of Cima; an area half a mile wide south of Baxter; the copper and silver mines in the New York Mountains; an area a few miles west of Barnwell; the northeast slope of Shadow Mountain, Silver Mountain mining district (Tucker and Sampson, 1943, pp. 413-414).

In 1955, fluorspar was discovered in the Orocochia Mountains, a few miles south of Shaver Summit, eastern Riverside County. Here several veins of fluorspar, ranging from a few inches to 6 feet in width, occur in shear and breccia zones in coarse-grained Mesozoic quartz monzonite. The veins are parallel and pinch and swell along their strike. The largest vein has been prospected intermittently along a strike length of 500 feet. Mine run fluorspar contains over 91 percent  $\text{CaF}_2$ , and a hand-picked sample was found to contain 97.83 percent  $\text{CaF}_2$ . The fluorspar meets all specifications for metallurgical uses, and a small shipment was made early in the spring of 1955 to the Kaiser Company at Fontana, California, for use in the blast furnace.

*Utilization and Specifications.* Fluorspar has several properties which promote its use in many industries. Because of its low melting point ( $1270^\circ$  to  $1387^\circ \text{C}$ ),





FIGURE 2. View of the Holmestake Mining Company's fluor spar prospect, Orocopia Mountains, Riverside County, California. The workings are on a large fluor spar vein which trends northeast, and is mostly 4 to 6 feet wide. The wall rock is coarse-grained Mesozoic quartz monzonite. Observer faces southwest.

its low viscosity when molten, and its ability to form eutectics, fluor spar finds wide application in many metallurgical processes. Fluor spar is also the source for fluorine in the manufacture of hydrofluoric acid which is important not only to the glass manufacturer but in the manufacturing of fluorine chemicals.

The principal use of fluor spar is as a flux in the basic open-hearth and electric furnace processes of steel manufacture. In 1953 the steel industry of the United States consumed about 287,607 tons of fluor spar, an average of about 6 pounds per ton of steel. Small amounts of fluor spar are used in refining gold, lead, copper, and antimony, and in the manufacturing of primary aluminum and magnesium.

Undesirable impurities in fluor spar intended for metallurgical use include silica, sulfur, and phosphorus. The last is seldom abundant enough to present much difficulty, but the amounts of silica and sulfur must be kept below 6 percent and 0.3 percent, respectively. The fluor spar must be free from fines and "reasonably free from barytes or zineblende, calcite, and limestone" (Dunham, 1952, p. 3).

Metallurgical-grade fluor spar should contain at least 85 percent  $\text{CaF}_2$ . Shipments of fluor spar analyzing between 80 and 85 percent  $\text{CaF}_2$  are subject to penalties, and if the material analyzes below 80 percent  $\text{CaF}_2$ , it will probably be refused. Similarly, penalties are usually assessed on any material containing more than 6 percent silica. Lack of supplies of metallurgical-grade fluor spar conforming to the desired specifications led some users to accept material of much lower grade during World War II.

About 38 percent of the fluor spar consumed in the United States is used in the manufacture of hydrofluoric acid. An exceptionally pure grade of finely ground (80 to 100 mesh) fluor spar is required in the process. Normally, the specification for acid-grade fluor spar calls for

a minimum of 97 percent  $\text{CaF}_2$ , with less than 1.0 percent each  $\text{SiO}_2$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$ , and  $\text{CaCO}_3$ , and no manganese, chromium, or sulfides.

Hydrofluoric acid was first utilized in the etching of glass, but it now has many other applications, and the demand for it continues to expand. "A range of compounds prepared from it includes fluorides of Na,  $\text{NH}_4$ , K, Mg, Ba, Al, Pb, Zn and Li for fungicides and for use in the light metal industry; bi-fluorides for etching; double fluorides with Al, Ti, Zn, and Be for metallurgy; siliconfluorides for lead plating and insecticides; and borofluorides for plating. Hydrofluoric acid is used in the production of synthetic organic compounds of fluorine and chlorine sold under the trade name of 'Freon'" (Dunham, 1952, p. 4), which is used in refrigeration and as a solvent and propellant for insecticides. A thermoplastic known as Teflon (polytetrafluorethylene) possesses a high degree of chemical resistance at temperatures up to  $250^\circ\text{C}$ . Artificial cryolite, used with natural cryolite in the production of aluminum by electrolysis, is prepared from impure acid-grade fluor spar. Anhydrous hydrogen fluoride is employed as a catalyst in the alkylation process for the manufacture of 100-octane gasoline and in the preparation of elemental fluorine.

Third in consumption of fluor spar is the ceramic industry which, in 1953, consumed slightly more than 38,000 short tons in the United States. Finely ground fluor spar is used to manufacture opalescent, opal, opaque, and colored glass. Fluor spar is an important constituent in earthenware glazes and opacified enamels. For these uses fluor spar, designated as ceramic-grade, must contain at least 95 percent  $\text{CaF}_2$ , less than 4 percent  $\text{SiO}_2$  and less than 0.14 percent  $\text{Fe}_2\text{O}_3$ .

A small amount of clear, transparent, nearly colorless fluor spar is used to manufacture lenses, especially those for use in microscopes. "For this purpose fluorite pieces must be at least  $\frac{1}{4}$ -inch in diameter, free from flaws,



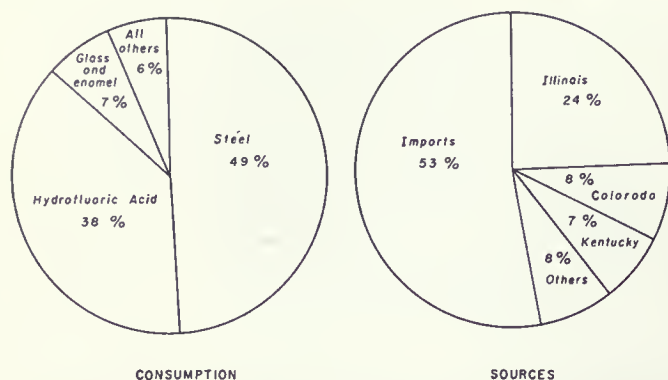


FIGURE 3. Fluorspar sales (domestic and foreign) to consumers in the United States, 1953, by consuming industry and by source, in percent.

and colorless or nearly colorless. Optical-quality fluorite usually exhibits a conchoidal fracture and is generally obtained from large crystals or cleavage octahedra from Great Britain" (Dunham, 1952, p. 5).

During World War II artificial fluorite crystals up to 6 inches across were produced under government contract for optical use. Minor amounts of fluorspar are consumed in making iron, ferroalloys, cement, and welding-rod coatings. One of the more important fluorine chemicals is uranium hexafluoride, used for the gaseous diffusion separation of the uranium isotopes  $U_{235}$  and  $U_{238}$ .

**Markets.** In 1953 the United States produced 318,036 short tons of fluorspar valued at \$15,736,321 and imported 361,219 short tons. About 20,000 short tons of fluorspar were consumed by industries in California. All of this fluorspar was shipped into California from sources in Nevada, Montana, and Mexico. At least 9,200 tons of fluorspar were consumed for metallurgical uses, 9,200 tons for the manufacture of hydrofluoric acid and aluminum fluoride, and 800 tons for the ceramic industry.

Metallurgical-grade fluorspar is marketed on the basis of "effective"  $CaF_2$  content. The effective  $CaF_2$  content of a fluorspar concentrate is calculated on the following basis: percentage fluorspar minus 2.5 times the percentage silica = effective  $CaF_2$  content. For example, a concentrate containing 85 percent fluorspar and 6 percent silica would have an effective  $CaF_2$  content of 70 percent ( $85\% - 2.5 \times 6\% = 70\%$ ).

In November 1955, metallurgical fluorspar containing 70 percent or more effective  $CaF_2$  was quoted at \$32.00 per short ton f.o.b. at the mine in Illinois and Kentucky. The same grade of fluorspar is being imported into the United States from Mexico and sold across the border at El Paso, Texas, at \$27.00 to \$29.00 per short ton, or

delivered to the consumer in San Francisco, California, from \$39.00 to \$41.00 per short ton.

The bulk of the acid-grade fluorspar imported into California is consumed by the Kaiser Aluminum and Chemical Company. The fluorspar comes from deposits in Nevada and is shipped to the General Chemicals Company for manufacture of aluminum fluoride for use by the Kaiser Aluminum and Chemical Company in the production of aluminum and chemicals. Acid-grade fluorspar containing not less than 97 percent  $CaF_2$  sold at \$47.50 per short ton f.o.b. mine in carload lots. The acid-grade fluorspar shipped in to California from Nevada sold for \$41.00 per short ton f.o.b. the mine. Ceramic-grade fluorspar containing not less than 94 percent  $CaF_2$  sold for \$65.00 per ton in paper bags f.o.b. the grinding plant.

Potential producers of fluorspar in California are faced with the problem of selling their fluorspar. As the Kaiser Steel Company and the Kaiser Aluminum and Chemical Company are the largest buyers of both acid- and metallurgical-grades fluorspar in California, they would be the firms most interested in new sources of supply. Substantial amounts of metallurgical-grade fluorspar are also consumed by other steel manufacturers in California who usually obtain their material from dealers in mineral raw materials. Several of these firms are: L. H. Butcher Company, Los Angeles, California; Brumley-Donaldson, San Francisco, California; and Industrial Minerals and Chemical Company, Berkeley, California. The potential producer of fluorspar would be required to meet the specifications set down by the consumer; the same as those discussed above.

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## GEM STONES

By LAUREN A. WRIGHT

The formal mining of gem stones in California has centered about the famous gem-bearing pegmatites in the Peninsular Ranges of San Diego and Riverside Counties. These deposits have yielded tourmaline, spodumene, beryl, topaz, quartz, and garnet, and have constituted one of the few notable sources of gem stones in the United States. At other localities in California, benitoite, chrysoprase, idocrase, jade, opal, and turquoise also have been mined in formal operations. Although the San Diego and Riverside County pegmatites alone have yielded gem and specimen material with a total value of at least \$2,000,000, the gem mining industry of California is small compared with other mineral industries of the state.

Gem mining in California was most active during the period 1890 to 1912; from 1880 to 1924 the state yielded about 23 percent of the gem material mined in the United States (Ball, 1937, p. 306). Although most of the mines have been idle in recent years, interest in the recovery of gem stones in California has increased markedly. This activity, however, is now undertaken mostly by thousands of hobbyists and week-end prospectors who have collected at many localities in the state. Statistics on the material thus obtained in California do not exist, but in 1953 its value constituted a significant proportion of the estimated value of \$500,000 to \$600,000 placed on the total gem stone production in the United States during that year (Thomson, et al., 1955).

### MINERALOGY AND GEOLOGIC OCCURRENCE

The term "gem stone" in its broadest sense is applicable to almost any mineral, rock, organic material, or synthetic material that can be used in the preparation of objects for personal adornment or for other ornamental purposes. In a more restricted sense, the term is applied to natural materials of unusual beauty that are both durable and rare. These commonly are grouped in three general categories—precious stones, semi-precious stones, and organic gem materials. The organic gem materials are pearl, coral, amber, and jet. Many gemologists, however, believe that the distinction between precious stones and semi-precious stone is too arbitrary to be valid, and point out that certain specimens of so-called semi-precious stones are more valued and hence more precious than some specimens of so-called precious stones.

Only certain varieties of three minerals—diamond, corundum (varieties ruby and sapphire) and beryl (variety emerald)—are customarily designated as precious stones, but some workers also include pearl and jade. The semi-precious stones are much more numerous, and, in general are relatively rare varieties of rather common mineral species. They consist mostly of gem varieties of (1) silicates, including andalusite, benitoite, beryl, idocrase, chrysocolla, diopside, enstatite, epidote, feldspar, garnet, jadeite, lazurite, olivine, phenacite, rhodonite, sphene, spodumene, topaz, tourmaline, tremolite, and zircon; as well as varieties of quartz, such as agate, amethyst, chalcedony, chrysoprase, citrine, jasper, onyx, rock crystal, rose quartz, and tiger's eye; and (2) oxides, in-

cluding anatase, cassiterite, hematite, opal, spinel and rutile. Semi-precious gem stones also include phosphates (apatite, lazulite, and turquoise), carbonates (azurite, calcite, malachite, and smithsonite) sulfate (gypsum), fluoride (fluorite), and sulfides (pyrite and sphalerite).

Diamond, corundum, and beryl have hardnesses of 7.5 (Mohs' scale) or greater, and hardnesses of 5 or more characterize most of the semi-precious stones. Some of the semi-precious group such as calcite, gypsum, and fluorite are much softer and their appeal stems from the pleasing appearance of certain varieties rather than durability. Most gem-quality materials are transparent or nearly so; but a few, including, azurite, chrysocolla, feldspar, jadeite, malachite, turquoise and the jasper variety of chalcedony, are translucent to opaque.

Some of the most valued gem stones occur as primary constituents of igneous rocks or in alluvial deposits derived from such rocks. The only known primary occurrences of diamond exist as disseminations in pipe-like bodies of an ultrabasic rock known as kimberlite. The most extensively mined of these deposits are in South Africa. Pegmatite dikes yield varieties of transparent beryl as well as gem-quality tourmaline, quartz, garnet, and spodumene. The world's best-known and most productive gem-bearing pegmatite areas are in Minas Geraes, Brazil.

Some gem stones occur in veins and as fillings of irregular cavities. Of these, opal, varieties of cryptocrystalline quartz, and turquoise are especially widespread and are mined in greatest volume. The last is believed to have been deposited largely or wholly from solutions of cold, descending water; the opal and quartz have been deposited mainly by ascending hot waters. In many places these minerals occur in volcanic rocks and probably are genetically related to them. Jadeite is a vein-forming mineral whose origin has been disputed but which commonly lies within or near bodies of ultrabasic intrusive rocks. The famous jade deposits of upper Burma are of this type.

Disseminated in metamorphic rocks are gem varieties of corundum (sapphire and ruby), garnet, and andalusite. Contact metamorphism has produced irregular masses of nephrite jade and lazurite which ordinarily can be shown to have replaced carbonate-rich rocks.

Because most gem stones are hard, durable, chemically inert, and have higher specific gravities than the common rock-forming silicate minerals, they resist weathering and become concentrated in residual soils and in stream and beach placers. Thus in many areas gem stones can be economically recovered from alluvial deposits where their bedrock occurrences either cannot be worked at a profit, or are worked at much greater expense. A very large proportion of the world's output of gem stones is derived from such deposits. Most of the ruby, sapphire and jade produced in the world are obtained from alluvial deposits in various parts of Asia, and much of the diamond production is recovered from alluvial deposits in South Africa.



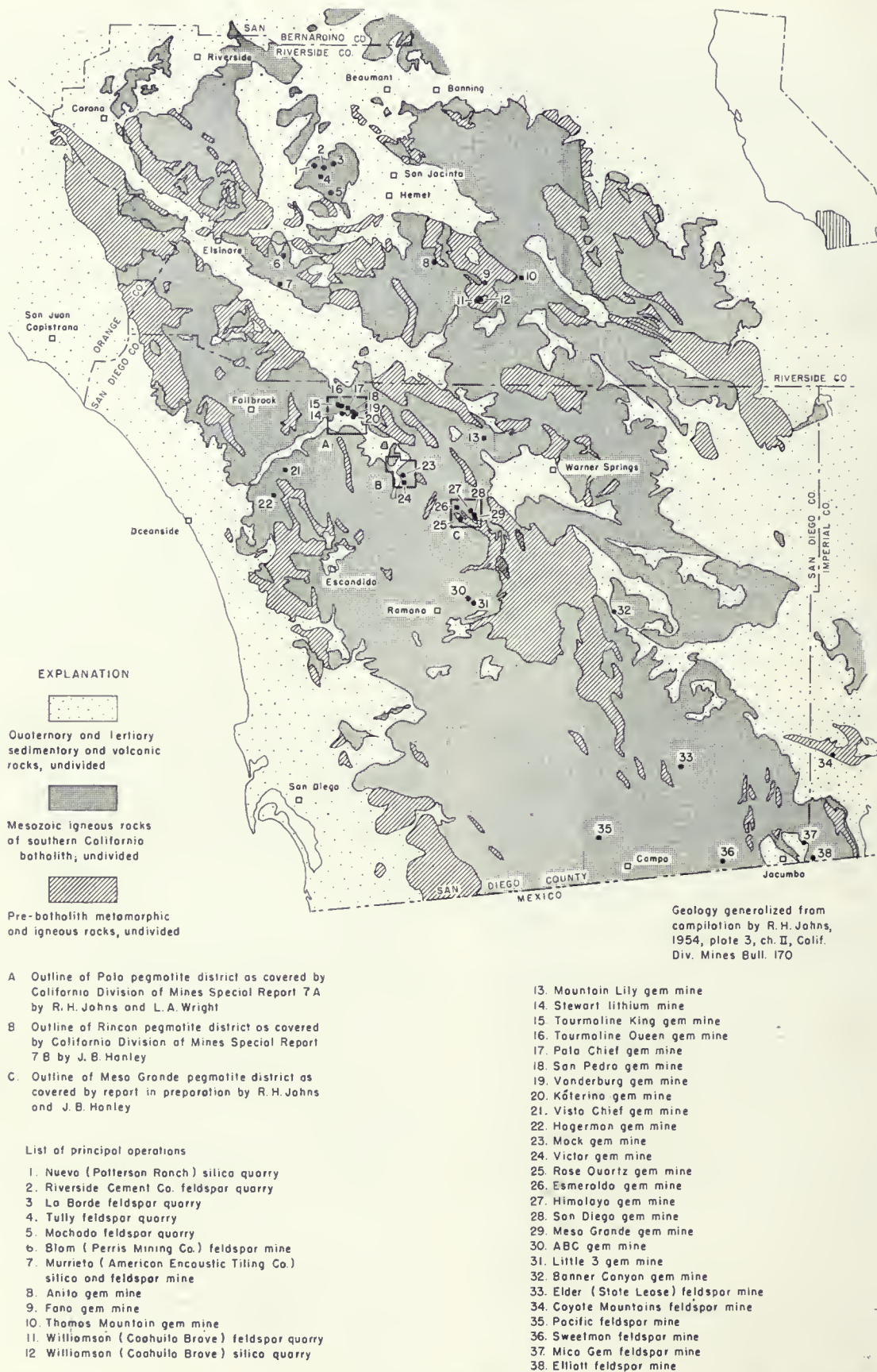


FIGURE 1. Generalized geologic map of the Peninsular Ranges province of southern California showing location of the principal gem-stone, feldspar, and silica mines in pegmatite bodies.



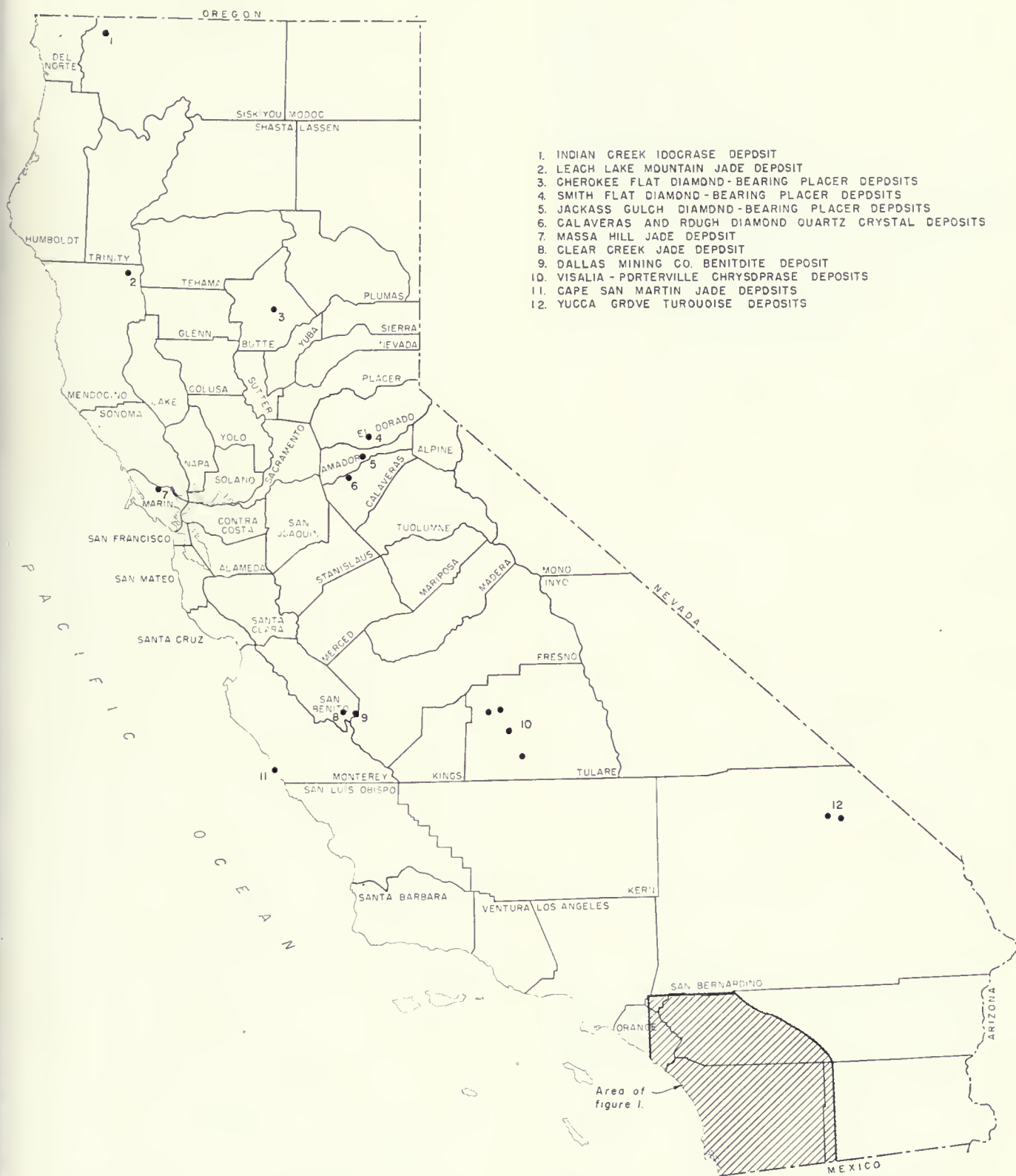


FIGURE 2. Index map of California showing locations of well-known gem-stone deposits that lie outside of the area of figure 1.



## LOCALITIES IN CALIFORNIA

Although gem mining in California has been sporadic and pursued on a small scale, hundreds of localities in the state have yielded minerals or rocks that fall under the broad classification of semi-precious gem stones, and even diamonds and near-emerald beryl have been found. In general, the best-known deposits are the ones whose development and operation have constituted serious mining ventures. Of these the tourmaline- and spodumene-bearing pegmatites of San Diego and Riverside Counties are by far the most numerous. Gem mining elsewhere in California has led to the recovery of turquoise and opal in San Bernardino County, benitoite from San Benito County, chrysoprase from Tulare County, idocrase from Siskiyou County, nephrite jade from Tulare County, and amethyst quartz from Lake County.

In California, gem stones also have been obtained from formal mining operations aimed primarily at the recovery of mineral substances for non-ornamental uses. Gathered in this manner have been gold-bearing quartz from gold lode mines, diamonds from gold placers, rhodonite from manganese mines, myrickite (cinnabar intergrown with chalcedony) from mercury mines, and howlite from borate deposits.

Whereas, in California, gem mining for profit has declined in recent years, gem hunting for pleasure has become a highly popular and well-organized activity. In 1956, the California Federation of Mineralogical Societies consisted of 107 member organizations with a combined membership of about 7,000 persons, most of whom regularly participated in collecting excursions. Most of the better-known collecting localities in California have been described in *Gems and Minerals*, the monthly official magazine of the Federation. To prevent the spoilage of some of the best and most frequented localities, the Federation has encouraged its member organizations to locate and legally to hold claims at these sites and to permit access to persons who wish to collect in moderation. Claims established and worked in this way are actually mines, in spite of their unrecorded production and unsystematic development by "volunteer" miners.

**Gem-Bearing Pegmatites of San Diego and Riverside Counties \***

*Distribution and General Features.* The most productive and most extensively developed of the gem-bearing pegmatites in California are exposed in a 25-mile belt that lies within San Diego County and embraces three pegmatite districts—one at Pala at the northwestern end of the belt, another at Rincon near the center, and a third at Mesa Grande at the southeastern end. Gem material also has been recovered from widely scattered pegmatites at Coahuila Mountain, Red Mountain and Thomas Mountain in western Riverside County, and in the Agnanga Mountain, Ramona, and Julian districts in San Diego County.

Of the gem-quality minerals in these deposits, tourmaline has been mined in by far the greatest quantity, and gem spodumene has proved abundant in certain of the lithium-rich pegmatites. The mining, which was aimed chiefly at the recovery of these two minerals and the non-gem mineral lepidolite (see section on lithium and

lithium compounds in this volume), also led to the recovery of gem varieties of quartz, beryl, topaz, and garnet.

All of the gem-bearing pegmatites of San Diego and Riverside Counties lie within the Peninsular Ranges province, a region underlain mainly by plutonic igneous rocks of the Southern California batholith and by pre-batholith metamorphic rocks. The pegmatite bodies were emplaced in late Mesozoic time during the end stages of the consolidation of the batholith. Most of them are within the dark-colored, more basic rocks of the batholith, especially in a unit known as the San Marcos gabbro.

Virtually all of the pegmatite bodies of the Peninsular Ranges province are elongate dikes. Although a given dike is generally rather uniform in thickness, some dikes are only a fraction of an inch thick, whereas parts of others are 100 or more feet thick. The thicknesses of those that contain most of the pegmatite, however, lie within the general range of 4 to 25 feet. Many of the dikes are 1,000 to 4,000 feet long. In some areas the dikes occur in swarms that have filled numerous closely spaced parallel to sub-parallel fractures.

The percentage of gem material in a given dike bears no obvious relationship to the average thickness of the dike. Indeed the dike at the very productive Himalaya mine at Mesa Grande averages only about 4 feet in thickness, whereas much larger dikes have yielded no gem material. Virtually all of the gem spodumene and significant amounts of other gem minerals, however, have been found within bulges in the dikes.

The dikes are granitic in composition. Large numbers of them consist wholly of graphic granite, but others are complex bodies of two or more rock units of contrasting texture or mineralogy or both. The gem and lithium minerals have been found in only a small proportion of the complex dikes and in none of the simple dikes.

Graphic granite forms most of the upper part of the typical complex dike, whereas its lower part contains a fine-grained quartz-feldspar (aplite) rock. Much of this fine-grained rock shows a distinct banding, caused by thin layers rich in minute grains of garnet or tourmaline, and is commonly known as "line rock."

Discoidal to pod-like masses of very coarse-grained pegmatite occupy the cores of many of the dikes and form the central parts of most of the bulges. Some of these masses consist of quartz-perthite or quartz-spodumene aggregates; others contain only quartz or perthite. In several of the complex dikes this coarse-grained pegmatite has been worked for feldspar or quartz (see sections on feldspar and quartzite and quartz in this volume). Irregularly distributed fracture-fillings and replacement bodies, composed chiefly of quartz, albite, and muscovite, are widespread in the complex dikes.

All of the gem-quality tourmaline, beryl, topaz, and garnet is contained in a type of pegmatite that is characterized by an abundance of well-formed crystals and lies within or near the cores of the dikes. It ranges from fine-grained to very coarse-grained and consists mostly of quartz, albite, orthoclase, and muscovite. It also contains concentrations of minerals rich in lithium, beryllium, boron, caesium, and other rare elements. This material is popularly known as "pocket pegmatite" because the crystals commonly are in pockets filled with

\* The data in this discussion have been obtained mostly from the following references: Jahns, 1948; Jahns and Wright, 1951; and Hanley, 1951; and from R. H. Jahns in personal communication.



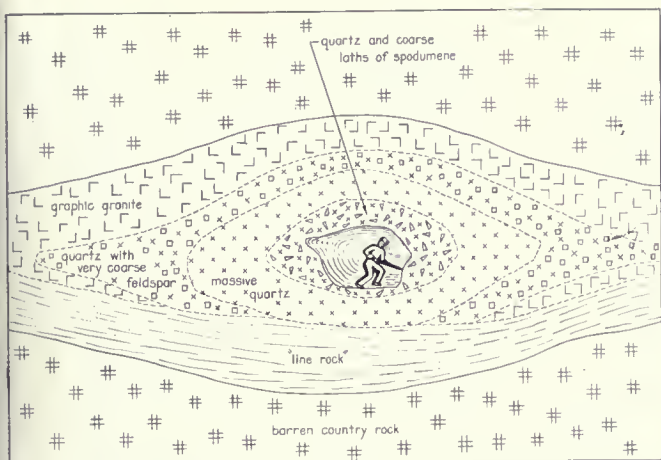


FIGURE 3. Idealized cross-section through a typical spodumene-bearing pegmatite in southern California. After R. H. Jahns, 1948.

red clay, but it rarely contains open space and much of it is clay free.

The gem tourmaline crystals are transparent prisms of the blue, pink, green, and colorless varieties. Nearly all gradations exist between these colors, and individual prisms commonly are bicolored or multicolored in concentric zones or in layers normal to their long axes. Most of the gem tourmaline occurs in prisms that are pencil-like in size and shape, but individuals as much as 4 feet long and 6 inches in diameter have been mined. Tourmaline is the most abundant and widespread gem mineral in the pegmatites of southern California, but a single source—the Himalaya mine in the Mesa Grande district—has yielded considerably more tourmaline than all of the other mines combined.

Spodumene, although locally abundant in the pocket pegmatite, is of gem quality only in the very coarse-grained, quartz-spodumene pegmatite. Here it occurs as unaltered residua in the central parts of some of the spodumene laths. The rest of the spodumene has been altered to a milky material composed partly or wholly of clay. In the pegmatites of the Southern California batholith, the gem spodumene is mostly of the pale-pink to deep bluish-lilac variety known as kunzite. A yellowish to colorless variety of spodumene is somewhat less abundant in these pegmatites and a pale-green variety is rare. The transparent spodumene ordinarily occurs in splintery, striated fragments less than 2 inches long, but locally these residual masses are as much as 4 inches wide and 15 inches long. Most of the gem spodumene mined in California has been removed from the Pala Chief, Katerina, and Vanderburg mines in the Pala district.

The most highly prized of the beryl gems in southern California pegmatites is a pale rose to peach-colored variety known as morganite. It is associated, in pocket pegmatite, with a nearly colorless to blue beryl. Both varieties occur in well-faced, equant to tabular crystals as much as 6 inches in maximum dimension. The gem beryl output has been obtained mostly from the Pala Chief, Anita, El Molino, and San Pedro mines in the Pala district, the Victor and Mack deposits in the Rincon district, and the Himalaya, San Diego, and Esmeralda mines in the Mesa Grande district.

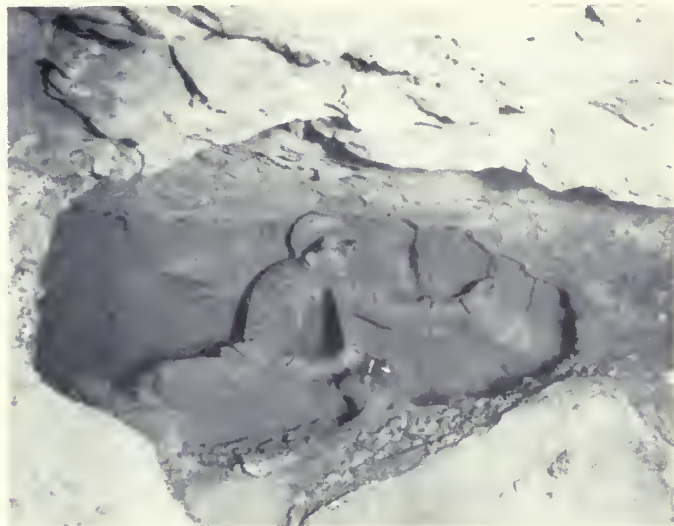


FIGURE 4. Part of underground workings at Pala Chief mine. This cavity yielded an exceptionally large concentration of gem spodumene. Photo by R. H. Jahns.

Transparent quartz, although less prized than the gem minerals noted above is abundant in many dikes and has been used in the fashioning of cut stones. Colorless to smoky quartz euhedra are abundant in pocket pegmatite, and anhedral masses of rose quartz occur in a few of the dikes. Most of the pocket quartz crystals are smaller than the milky anhedral crystals that are abundant in the cores of the dikes, but locally they are as much as 2 or 3 feet long.

Gem topaz and gem garnet, also constituents of pocket pegmatite, are rarer than the gem stones noted above. The topaz ranges from colorless through pale green to aquamarine, and occurs in well-developed prisms as much as 4 inches long. The colored topaz is rare and most of the crystals are less than an inch long. Gem topaz has been recovered most abundantly from the Mountain Lily time at Aguanga Mountain and from the Little Three and A.B.C. mines near Ramona. The gem garnet, mostly spessartite, ranges in color from golden yellow to cinnamon brown, and occurs as dodecahedrons about an eighth of an inch to three-quarters of an inch in diameter. The Little Three and A.B.C. mines have been the principal sources of gem garnet.

**Mine Workings.** Approximately 90 percent of an estimated 200,000 to 300,000 pounds of gem and near-gem material recovered from the pegmatites of southern California has been obtained from only five mines—the Himalaya and San Diego in the Mesa Grande district and the Pala Chief, Tourmaline Queen, and Katerina in the Pala district (fig. 1). All but a very small part of the remainder has been removed from ten other mines—the San Pedro, Tourmaline King, and Vanderburg in the Pala district; the Esmeralda and Mesa Grande in the Mesa Grande district; the A.B.C. and Little Three mines near Ramona; the Mountain Lily at Aguanga Mountain; and the Anita near Red Mountain and the Fano at Coahuila Mountain (fig. 1). About 35 small and widely scattered, additional mines also have yielded gem material, and two to three times as many deposits have been seriously prospected.



The development of most of the mines began with the discovery of gem crystals in pegmatite outcrops or in the float downslope from them. Some workings were started only on bulges in dikes whose exposures were barren of gem material or nearly so. In their early stages most of the mines consisted of open cuts from which shallow underground workings were developed as the mining advanced. In all but a few of the mines the gem production was obtained from only a single pocket. In each of the five most productive mines, however, numerous pockets were encountered.

The mine workings are typically very irregular and most of them range from a few feet to several hundred feet in total length. They were driven through the pegmatite rock that was believed to hold the most promise for gem production, principally along the upper margin of the "line rock" or in the lower or central parts of the cores of coarse-grained pegmatite. The Himalaya and Tourmaline King mine workings, each of which extend down-dip for nearly 200 feet, probably are the deepest penetrations.

The drilling has been done mostly by hand, and, in general, care has been taken in blasting so that as little as possible of the gem material is fractured. Some of the workings remain wholly accessible, but entry to others has been made difficult or impossible by caving and back-filling.

*History of Mining Operations.* That the gem stones of San Diego and Riverside Counties were gathered and prized by Indians long before they were discovered by white men is shown by the existence of tourmaline crystals in ancient burials. The first recorded discovery, however, was made by Henry Hamilton in 1872 when he noted tourmaline fragments on the slopes of Thomas Mountain in Riverside County and traced them up-slope to a pegmatite dike that was later developed by the Thomas Mountain mine. Subsequently, other minor occurrences of gem stones were noted in this area.

The next significant tourmaline discovery became known in 1892. This was at a locality near Pala and now occupied by the Stewart mine. Other discoveries of tourmaline in the Pala district soon followed, but were overshadowed in 1898 when the very rich tourmaline deposits at Mesa Grande were first mined.

In 1902, Fred M. Sickler, while working the Katerina mine near Pala, encountered gem spodumene, a very rare material whose occurrence here attracted the attention of mineralogists the world over. Most of the gem spodumene recovered at Pala proved to be colored various shades of pink and lilac, and soon after its discovery, was named "kunzite" (Kunz, 1903; and Baskerville, 1903) a new gem variety that became popularly known as "California's own gem". Kunzite, however, has since been recovered commercially in both Brazil and Madagascar.

Intensive mining in the Mesa Grande area was confined mostly to the period 1900-10, and in the Pala area mostly to the period 1903-14. As many as 70 mines and prospects were being worked at one time and at least 95 percent of the gem output of San Diego and Riverside Counties was obtained in the 1900-14 interval. By a coincidence fortunate to the mine operators, the discovery and development of these deposits came at a time

of high tourmaline prices which were brought about largely by the popularity of this gem in China. The fall of the Chinese dynasty in 1912, however, caused this market to dwindle to insignificance and the resulting drop in price contributed to the virtual discontinuance of profitable gem mining in this region. Moreover, by 1914 most of the readily detected and easily worked gem occurrences had been well exploited, and the discovery of additional gem-bearing pegmatites at most mines had become, in the opinion of the operators, prohibitively expensive. Nevertheless, the recovery of gem stones from the pegmatites of the Peninsula Ranges province has continued from 1914 to the present, albeit irregularly and on a considerably smaller scale than before. Much of this later mining has been the work of persons as much or perhaps more attracted by the romance of gem mining than by possible monetary gain.

Operations at the Tourmaline King mine near Pala continued into the 1920's, and in this later development the pegmatite dike was thoroughly explored by 1,000 feet or more of underground workings; but only a very small amount of tourmaline was added to its previous production. A small output of byproduct tourmaline and beryl was obtained in the removal of lepidolite from the Stewart mine which was last worked in 1928. The Himalaya mine has been reopened on several occasions since it was shut down in 1914, but with generally poor rewards. The most productive of these later Himalaya operations began in 1952 and was continuing in 1956. Since 1930, sporadic development in excess of assessment work also has been undertaken at the Katerina, Vanderburg, San Pedro, Fargo, and White Queen mines near Pala, and at the Rose Quartz, Esmeralda, and San Diego mines at Mesa Grande.

The production records of most of the mines, unfortunately, are incomplete and are inconsistent with respect to the values placed by the operators on the various types and grades of gem stones. Moreover, a large but undetermined proportion of the total output has been removed surreptitiously by miners, both during and after regular working hours and from both active and otherwise inactive mines. Another but much smaller fraction of the total gem output has been removed by amateur mineral collectors whose search has been confined almost wholly to mine dumps.

The output of the Mesa Grande district, which has been by far the most productive of the gem-bearing areas of California, has been estimated at "nearly a quarter of a million pounds of tourmaline valued nearly \$800,000, and a much smaller output of quartz, beryl, and other gem minerals . . . valued at about \$14,000" (Jahns and Hanley, 1955). The Himalaya mine, with an output that probably totals 150,000 to 200,000 pounds of gem tourmaline and several hundred pounds of gem beryl, has been by all odds the most productive gem mine in California, and still is unsurpassed in the world as a source of gem tourmaline.

Available records indicate that the Pala district has yielded 2,980 pounds of gem tourmaline valued at \$154,500; 1,325 pounds of gem spodumene valued at \$152,900; and 460 pounds of other gem minerals, largely quartz and beryl of non-gem quality, valued at \$11,800. These figures are incomplete and the actual output, particularly of tourmaline, quartz, and beryl, may have been



considerably higher. Most of the gem spodumene output was obtained from the Pala Chief mine, which remains the world's chief source of this material.

The gem production of the Rincon district probably totals less than \$2,000 in value, represented chiefly by beryl, whereas pegmatites outside of the principal belt have contributed gems with an estimated total value of several tens of thousands of dollars.

#### Other Gem Operations

**Benitoite.** Benitoite ( $\text{BaTiSi}_3\text{O}_9$ ), a mineral found only in California, is noted not only for its beauty, but for its unique crystal habit; it is the only representative of the trigonal class, hexagonal system. It was discovered in 1907 in San Benito County at a locality on the west side of the Diablo Range and 25 airline miles north of Coalinga. Except for a few sedimentary grains obtained from drill holes in the Lost Hills area of Kern County, no other occurrences of benitoite have been recorded.

The benitoite in the Diablo Range occurs with the black mineral neptunite ( $(\text{Na},\text{K})_2(\text{FeMn})(\text{Si},\text{Ti})_5\text{O}_{12}$ ) in veins of massive white natrolite ( $\text{Na}_2\text{Al}_2\text{Si}_3\text{O}_{10} \cdot 2\text{H}_2\text{O}$ ). The veins lie in body of highly fractured metamorphic rock, composed partly of mica schist and partly of massive metagabbro (?), which occurs as a large inclusion in serpentine (Loudenback and Blasdale, 1909, pp. 331-380; Sterrett, 1911a, pp. 742-748). The benitoite-bearing natrolite has been removed from a zone about 230 feet long, but the veins proved to be most abundant in a lenticular shoot, 25 feet or more in maximum thickness. The veins range in thickness from a small fraction of an inch to about 2 inches. The benitoite, which is most abundant in the thicker veins, occurs in well-formed, transparent, colorless to sapphire blue, flattened prisms which are mostly one-eighth to half an inch wide. The largest are about  $1\frac{1}{2}$  inches wide. As most of the crystals are minutely fractured, the output was sold largely as specimen material.

The deposit was most actively worked by the Dallas Mining Company during the period 1907-09. It has been developed by a large open cut and by about 125 feet of underground workings driven mostly during the original period of operation (Averill, 1947).

**Chrysoprase.** Chrysoprase, a green variety of chalcedony, was discovered in 1878 at Venice Hill, 8 miles east of Visalia, Tulare County. By 1898, it also had been discovered at other localities in the county, including one 8 miles southeast of Porterville, and two near Lindsay (Sterrett, 1911a, pp. 751-756; Kunz, 1912, pp. 154-155).

At each of these four localities chrysoprase occurred in narrow veins from a small fraction of an inch to 2 or 3 inches thick. The veins were irregularly distributed in serpentine and were associated with a red and brown jasper. The chrysoprase ranged from a pale green, opaque and generally subcommercial chalcedony to a beautifully translucent emerald green material which commanded the highest prices. At depths of about 20 feet, the chrysoprase was found to grade downward into milky white chalcedony. The chrysoprase and the related siliceous rocks are believed to have formed during the weathering of the serpentine, and the green color to have been derived from near-surface concentrations of nickel.

At one time or another, during the period 1878 to 1911, at least five chrysoprase mines were active in Tulare County; but all of them eventually were shut down, partly because chrysoprase as a gem stone had waned in popularity, and partly because most of the better, easily recovered material had been removed. The mining operations consisted mainly of open cuts, but included a few shallow underground workings.

**Diamond.** An estimated 400 to 500 diamond specimens have been recovered from placer deposits throughout the western foothills of the Sierra Nevada and in Del Norte, Humboldt, and Trinity Counties (Murdoch and Webb, 1948, pp. 129-132). All were chance discoveries made largely during placer gold operations prior to 1920. The most productive of these deposits is at Cherokee Flat in Butte County and has yielded at least 300 diamonds. Other noted localities are at Jackass Gulch near Volcano, Amador County; and at Forest Hill, Placer County, and Smithflat, in El Dorado County.

Some of the diamonds are white and transparent, but most show a yellow tinge. Only a few exceed 2 carats in weight. They have been gathered mostly from Recent placer deposits, but at Smithflat they were recovered from placers in Tertiary channels (Schaller, 1916, pp. 848-849). All apparently were derived from bodies of ultrabasic rock in the areas tributary to the placer deposits. Primary occurrences of diamond in California remain to be verified, although such material was actively sought by a mining company in the early nineteen-hundreds. The most extensively prospected area lies about a mile north of Oroville, Butte County. Here a body of rock, which was believed to be identical with the diamond-bearing kimberlite of South Africa, was developed by numerous pits and two shafts 300 feet and 60 feet deep. No production was recorded, and the rock proved to be eclogite (Sterrett, 1911a, pp. 759-761; 1911b, pp. 859-860; Murdoch and Webb, 1948, p. 132).

**Idocrase (Vesuvianite).** Californite, a massive, compact variety of the mineral idocrase (a basic calcium-aluminum silicate) has been found at several localities in northern California. The best known and most productive deposits lie about 10 miles north of Happy Camp, Siskiyou County, but deposits of californite also have been mined or seriously developed near Pulga in Butte County, near Hawkins schoolhouse (Watts Valley) and near Selma in Fresno County, and at two localities in Tulare County, one near Lindsay and the other near Exeter (Kunz, 1905, pp. 93-95; Sterrett, 1911a, pp. 749-751; 1911b, 855-858; 1912, pp. 1043-1046).

All of the deposits consist of veins, lenses, or pods in serpentine and contain californite that is characteristically highly fractured and shows a marked range in color from dark green to gray. The highest quality material is bright emerald green or grass green and translucent to transparent. It closely resembles jade and at first was mistaken for this gem. The name californite was first applied by Kunz (1905, p. 95) to such material obtained from the Happy Camp locality.

Near Happy Camp, the californite was mined from pods and lenses along a 300-foot zone in serpentine and from float derived from this zone. The largest individual body was about 10 feet thick and the float fragments were as much as 6 feet in maximum dimension. A high



degree of fracturing, however, caused much of the material to be of non-gem quality. This deposit was discovered in 1900 and was worked for about 11 years. Mining was confined mostly to open pits; underground exploratory work failed to encounter enough commercial material to permit extensive underground operations.

As the market for californite diminished and the unflawed material became more difficult to recover, formal mining dwindled, and, since 1911, californite production has been almost wholly the work of mineral collectors.



FIGURE 5. Jade blocks being sawed at quarry of Covelo Jade Mines, Inc., Leach Lake Mountain, Mendocino County. Photo by C. W. Chesterman.

**Jade.** The occurrence in California of both types of jade—jadeite (a distinct mineral species) and nephrite (a compact, fibrous tremolite-actinolite)—was known as early as the 1930's, but most of the discoveries of jade in place have been made subsequent to 1946. Nephrite was first discovered in California in the form of pebbles distributed along the beach at and near Cape San Martin in southern Monterey County. By 1947, several exposures of nephrite-bearing bedrock had been noted nearby (Crippen, 1951). In 1949, nephrite also was discovered near Porterville, Tulare County, near Petaluma, Marin County (Chesterman, 1951), and at Leach Lake Mountain in Mendocino County. In the mid-1930's, jadeite was discovered in southwestern San Benito County (Meilenz, 1936). This was the first occurrence of this mineral to be noted in the western hemisphere, but it has since also been found at localities in the Coast Ranges in Mendocino, Sonoma, and San Luis Obispo Counties (Yoder and Chesterman, 1951, p. 6).

Both jadeite and nephrite occur as lenses, pods, and veins within or near bodies of serpentine. The largest of the known nephrite bodies in the Cape San Martin area is a pod at least 15 feet long (Crippen, 1951), whereas the jadeite bodies of San Benito County are as much as 200 feet long and 50 feet wide. Few of the jade deposits thus far discovered in California, however, exceed a few feet in maximum dimension. The jade ranges in color from white through pale green to dark grayish green or dark bluish green and is generally semi-opaque. Only a small proportion of the material recovered to date is of good gem quality, and none shows the apple-green color and near-transparency of the better Burmese jade.

The Cape San Martin and southwestern San Benito County localities each have yielded several tons or more of jade, but most of this output has been obtained from placer deposits. The Leach Lake Mountain jade, which actually is a nephrite-jadeite mixture, has been recovered from both placer and bedrock deposits. In 1956, jade from this area was being sawed into slabs, exported to Germany, and then carved into art objects (C. W. Chesterman, personal communication, 1956). The jade deposits at Petaluma and Porterville are in bedrock and also have been worked on a small scale.

**Quartz Crystal.** Gem-quality quartz crystals, already noted as occurring in the pegmatites of southern California, have been gathered at many other pegmatite and non-pegmatite deposits in the state. Of these others, only the placer deposits at Chili Bar, Calaveras County, have been seriously mined for gem or ornamental material. Some of the yield from the two mines at this locality was marketed for optical or piezoelectric uses, and the deposits are discussed in the section on quartz crystal in this volume.

Among the other better-known gem quartz crystal localities in California are the Fiddletown, Oleta, and Volcano areas in Amador County; Cerro Gordo mine area and Deep Springs Valley, Inyo County; Clear Lake Highlands, and Howard Springs, Lake County; the Hornitos area, Mariposa County; and the California Hot Springs, Lemon Cove, and Exeter areas in Tulare County.

**Turquoise.** All but a very small part of the turquoise produced in California has been obtained from two areas, each in San Bernardino County. By far the more productive were deposits in a 9-mile belt that extends westward from Yucca Grove. The other area lies 2 miles east of "Cottonwood Siding on the Santa Fe Railroad" (Sterrett, 1911a, p. 780).

The deposits near Yucca Grove are grouped about three localities—one at each end of the belt and a third in the middle. The turquoise occurs as irregularly distributed smears, veinlets, and nodules in alteration zones within granitic rocks and associated with quartz veinlets and alunite (Kunz, 1905, pp. 107-110; Sterrett, 1912, pp. 1011-1073; Wright, et al., 1953, pp. 165-166, 149-150). These occurrences were mostly a fraction of an inch thick, but some were as much as 1½ inches thick. The turquoise ranged in color from pale blue to greenish blue and much of it yielded excellent gem material.

As the mineralization was widespread and apparently did not extend to depths greater than 100 feet, the deposits were developed by numerous open pits and shallow underground workings. They previously had been worked by prehistoric Indians and were rediscovered in 1897. Although intensively worked for several years, the mines were shut down in 1903 when the known reserves of the higher quality material were depleted.

The deposit near Cottonwood Siding was developed by the Cove Turquoise mine which was active at some time during the period 1903-09. Here the turquoise occurred as seams and nodules within a zone, probably no more than 450 feet long, along a contact between metagraywacke and metarhyolite (Sterrett, 1911a, p. 780). The turquoise, which ranged from pale blue to moderately



dark blue, was mined by means of small pits and shallow underground workings.

*Miscellaneous Gem Stones.* Deposits of agate, jasper, and petrified wood have not supported continuing and profitable mining operations in California, but these varieties of silica are more abundant and widespread in the state than any of the other materials commonly classed as gem stones. Consequently, they have been gathered in the greatest volume and have been the most actively sought by amateur mineralogists and lapidarists. Especially fine material has been gathered near Coalinga, Fresno County; in the Castle Butte-Boron, Cache Creek, Last Chance Canyon, Red Rock Canyon, and Rosamond Hills areas of Kern County; at Stone Canyon, Monterey County; the Chuckwalla Mountain-Wiley Well region, of Riverside County; in the Cady Mountains, Calico Mountains, Eagle Crags-Lead Pipe Springs region, Opal Mountains-Black Mountain area, and the Owl Hole Spring area in San Bernardino County; near Nipomo in San Luis Obispo County; and near Morgan Hill in Santa Clara County.

Rhodonite ( $\text{MnSiO}_3$ ) of gem or near-gem quality has been obtained near Fiddletown, Amador County; near Randsburg and in the Rosamond Hills, Kern County; in the Lancaster area, Los Angeles County; near Taylorsville and in Genessee Valley, Plumas County; and near Jacumba, San Diego County. Opal was mined briefly in the Opal Mountain area northwest of Barstow in San Bernardino County.

Among the other localities in California from which gem or ornamental stones have been obtained are Garnet Hill (garnet and epidote) in Calaveras County; Lower Panamint Valley and Furnace Creek Wash (travertine), Inyo County; Chowchilla-Daulton area (chiarolite), Madera County; Warner Range (obsidian), Modoc County; White Mountains (andalusite and lazulite), Mono County; and Cuyama Valley (alabaster), Ventura County.

#### UTILIZATION AND TREATMENT

Although by definition gem stones are used for personal adornment or other ornamental purposes, much gem-quality material is not thus employed. Some is retained, uncut, in mineral collections, and some is used for industrial purposes. Agate, for example, is employed in the manufacture of mortars, pestles, and spatulas; transparent, unflawed, and untwinned quartz crystals are made into piezoelectric oscillator plates, and various optical devices; and off-color or very small diamonds are valued for their abrasive quality (see sections on quartz crystal and abrasives in this volume). Natural gems have been employed as jewel bearings in timepieces and scientific instruments, and garnets mined from the pegmatites near Ramona, California, are still thus used. Most jewel bearings now consist of synthetic sapphires and rubies.

The cutting of precious gems is largely the work of skilled professional lapidaries whereas most of the cutting of semi-precious stones is now done by hobbyists. A growing number of amateur lapidaries, however, are fashioning gem stones whose quality is comparable with or exceeds that of the average commercial worker.

The professional faceting of quality gem stones is done mostly outside of the United States, especially in Germany and Brazil. Gem fashioning in California centers

about the thousands of home cutting shops. Although numerous professional lapidaries are employed in the state, they work in small shops, and few of them are seriously occupied with quality cutting. Instead, they are involved mainly in special order work consisting mostly of fitting and trimming of stones and replacing damaged stones.

The oldest and still most-used type of cut, known as the cabochon, is prepared simply by rounding and polishing the specimen. It is best suited to opaque or translucent gem stones whose appeal lies in color, sheen, opalescence or asterism. The facet cut, which consists of numerous flat surfaces, is best for transparent gems. Facet types have been developed mathematically to provide a maximum brilliance for given indices of refraction and degrees of dispersion. In order to obtain the largest possible cut stone from a given specimen, lapidaries commonly (and regrettably) deviate from the optimum orientation of facets, and thereby lessen the brilliance.

An inexpensive tumbling technique, which applies a high polish to irregularly shaped gem-stone fragments, was introduced in the late 1940's and has since become widely used. The simplicity of the technique and the popularity of jewelry made from such stones has caused a marked increase in the output of polished gem stones in California. A typical tumbling apparatus consists of a motor-driven rotating barrel, circular or hexagonal in cross-section, and a foot or two in diameter. The charges, whose volume is about one-third that of the barrel, consist of the gem stone fragments, abrasive or polishing agents, and various additives.

#### MARKETS

The crude gem stone material that has been found in California, as elsewhere, command prices that range widely and are determined by (1) the mineral species and variety, (2) the size and quality of the individual specimens, and (3) popularity of the material at the time of sale. Much of the gem trade is handled on the basis of barter between hobbyists or by part-time lapidaries and is outside of the ordinary commercial channels. A market also is provided by the many professional gem and mineral dealers that are established in California, but such dealers ordinarily are interested only in the highest quality material and trade mostly in gem minerals from out-of-state sources.

In common practice, the operators of small domestic gem mines have separated newly mined material into three categories: (1) "gem" material from which unflawed gem stones, preferably larger than 5 carats, can be cut; (2) "specimen" material not adaptable to cutting, but attractive enough to be valued by serious collectors; and (3) "pound" material of low commercial value. They then have marketed the three grades to individual collectors, to gem dealers, or to lapidary supply houses at prices consistent with grade and popularity.

Previous to the late 1940's, only the very highest quality specimens of the chalcedony-type gem stones entered into the formal trade. The development of new tumbling techniques, however, has permitted the profitable treatment of much of the material that had been considered sub-commercial, but the uncut material remains very low in price and difficult to market.



Much of the high-quality material eventually has been sent out of the United States for faceting. The development of a large domestic gem-cutting industry is hindered by the high cost of labor and the existence of an over-supply of most gem stones on the domestic market. The demand for unusually well-cut stones, however, is high. Listed below are the 1956 retail prices for average quality cut stones of the types mined or collected in California.\*

**Tourmaline:**

- green, 6-10 carat stones, \$4-\$15 per carat;
- pink, 6-10 carat stones, \$2-\$6 per carat.

**Spodumene:**

- kunzite, 5-15 carat stones, \$6-\$12 per carat;
- pale green variety is priced somewhat lower than kunzite.

**Beryl:**

- yellow to pink, 3-6 carat stones, \$2-\$8 per carat.

**Garnet:**

- pale yellow grossularite, 5-10 carat stones, \$3-\$8 per carat.

**Topaz:**

- colorless to very pale colored, 5-10 carat stones, \$2-\$8 per carat.

**Benitoite:**

- all shades, 1 carat sizes, \$15 to \$25 per carat (very few stones available).

**Jade:**

- Californite, \$1-\$8, per cabachon stone of average size.
- Jadeite, \$2-\$12 per cabachon stone of average size.
- Nephrite, \$4-\$20 per cabachon stone of average size.

**Turquoise:**

- 20¢-50¢ per carat in cabachon stone of average size.

**Chrysoprase:**

- \$2-\$8 per cabachon stone of average size.

**Chalcedony (varieties agate, jasper, petrified wood, etc.):**

- \$2-\$8 per cabachon stone of average size.

**Rhodonite:**

- \$2-\$8 per cabachon stone of average size.

- |         |   |  |
|---------|---|--|
| Diamond | } | quantity from California is too small to be subject to a recognized price range. |
| Opal    |   |  |
| Epidote |   |  |

As these prices apply to the retail trade, those paid by dealers are considerably lower.

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\* These prices and most of the data in the foregoing discussion of utilization and treatment were kindly supplied by Mr. James W. Coote of the Gemological Institute of America, 11940 San Vicente Boulevard, Los Angeles 49, California, and 5 East 47th Street, New York City.

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## GOLD \*

BY WILLIAM B. CLARK

Gold, to most people, is California's best-known metallic mineral commodity. It was the principal attraction to early-day settlers and has continued to stimulate the growth of California. During the period 1848-1954, California mines yielded 103,000,000 fine ounces of gold valued at more than 2½ billion dollars, a total exceeding that of any other state. For many years the annual gold output of California was the highest of all mineral products of the state; but in 1907, gold was surpassed in value by petroleum and more recently by several other mineral commodities. Gold continued to be the state's most valuable metallic commodity until World War II. In 1943, it was surpassed by quicksilver, in 1944 by tungsten, and since 1952 by both tungsten and iron.

The curtailment of gold mining during World War II caused a pronounced reduction in gold output from 1942 to 1945. Following World War II, gold production rose to an output of 431,415 fine ounces in 1947. However, since 1947 gold output has followed a diminishing trend. This trend is attributable to the fixed price of gold (\$35.00 per ounce), the high cost of labor and supplies, the expense of reconditioning shut-down mines, and the depletion of many of the workable gold deposits, particularly dredging ground.

*Mineralogy and Geologic Occurrence.* Native gold is by far the most abundant of the gold minerals. In nature it is commonly alloyed with silver, and the alloy is known as electrum if the silver content exceeds 20 percent. The silver fraction in California gold averages about 12 percent; electrum is relatively rare in the state. The purity of gold is usually expressed in fineness. Pure gold is 1,000 fine. Gold that is 900 fine contains 900 parts of pure gold in every 1,000 parts of the sample or alloy. The gold mined in California ordinarily lies within the 700 to 900 fineness range.

Gold crystallizes in the isometric system, but ordinarily is massive or flaky. Although crystals are uncommon in most gold deposits, well-formed crystals are abundant at several lode mines in California. Such crystals generally are distorted into leaf-like aggregates. Ordinarily gold is disseminated in microscopic grains through the enclosing rock. In many high-grade ores it occurs in visible threads and plates and locally forms masses.

The tellurides, calaverite ( $\text{AuTe}_2$ ), sylvanite ( $\text{Au,Ag}(\text{Te}_2)$ ), and petzite ( $\text{Au,Ag})_2(\text{Te})$ , have been noted at only a few locations in California but are of little commercial significance in the state.

Most primary gold deposits are closely associated with intrusive rocks of acidic or intermediate composition. Many of the California deposits consist of gold-bearing quartz veins that contain various proportions of pyrite. Such deposits have formed in fissures or as cavity-fillings and have been deposited by aqueous solutions. Some gold deposits are the products of contact metamorphism or replacement. Gold also is commonly disseminated in in copper, lead, and zinc ores. Because of its high specific gravity and resistance to weathering, gold is easily concentrated in placer deposits.

*Lode Deposits of the Western Sierra Nevada.* The chief gold-bearing region in California is the west slope of the Sierra Nevada. The most productive deposits in this region have been in the Mother Lode belt, the Grass Valley-Nevada City district, the Tertiary channel gravels, and the Quaternary stream gravels.

The Mother Lode is a northwest-trending system of veins traversing the hills of the western Sierra Nevada. It is about 120 miles long, a mile wide, and extends from Mariposa County to northern El Dorado County. It consists of an en echelon to linked system of steeply dipping veins which occur as fissure fillings within or close to a system of reverse faults. The system cuts metamorphic rocks of sedimentary, volcanic, and intrusive igneous origin, and for much of its length separates Paleozoic from Jurassic rocks.

Although certain features are characteristic of all Mother Lode gold deposits, other features differ greatly. Two main types of gold deposits characterize the Mother Lode—gold-quartz veins and bodies of mineralized country rock. Productive quartz veins are characteristic of the north portion of the Mother Lode, and mineralized country rock associated with large barren quartz veins and mariposite-ankerite rock are most common in the south portion (Knopf, 1929, p. 23).

The quartz veins are tabular masses that are discordant with the planar features of the enclosing rock. The quartz is massive or exhibits a ribbon structure. It generally is associated with fault gouge. The gold is disseminated in the veins in the free state and is closely associated with pyrite, which comprises 1 to 2 percent of most ore bodies, and with other less abundant sulfides. The veins range from less than one foot to as much as 50 feet in width, and are as much as several thousand feet in length.

The ore shoots are relatively small in longitudinal dimension, and stope lengths average 200 to 300 feet (Knopf, 1929, p. 26). Some shoots extend to much greater depths, however. The Argonaut mine in Amador County, for example, has been successfully worked to an inclined depth of 6,300 feet. Not all of the ore shoots crop out at the surface, and each deposit contains much barren rock. Vein junctions and intersections are favorable locations for ore shoots. Most of the Mother Lode gold-quartz ore has been of moderate grade, and has averaged from 10 to 20 dollars per ton.

Mineralized greenstone, which is known as "gray ore," commonly is associated with the gold-quartz veins, and in some deposits it comprises the entire ore body. Gray ore is composed of ankeritized greenstone and contains pyrite and arsenopyrite which comprises 3 to 4 percent of the rock. The gold is disseminated in the greenstone and is closely associated with the sulfides. In the Mother Lode belt, immense bodies of mineralized schist, that contain only a few dollars per ton in gold, have been mined at Carson Hill, Calaveras County and at Georgia Slide, El Dorado County. At Georgia Slide, where the gold deposits are known as "seam diggings," the gold occurs in quartz veinlets in deeply weathered schist.

\* Partly extracted from a section by C. A. Logan in California Div. Mines Bulletin 156.



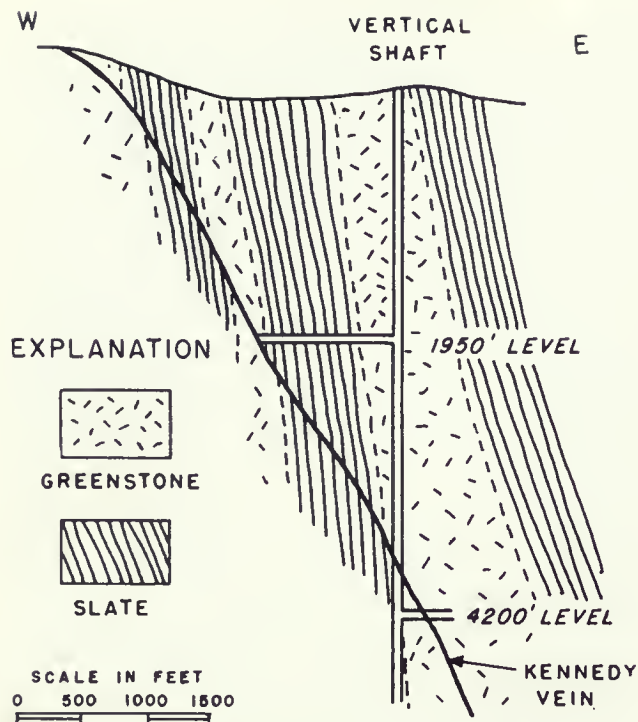


FIGURE 1. Generalized section through a Mother Lode gold mine, the Kennedy mine in Amador County, showing fault displacement of slate along the vein. (After Knopf, 1929, p. 64.)

The most productive part of the Mother Lode has been a 12-mile segment between Jackson and Plymouth in Amador County. Here, the chief mines with their approximate production in dollars are as follows: Kennedy, 34 million; Argonaut, 25 million; Keystone, 24 million; Old Eureka, 19 million; Central Eureka, 17 million; and Plymouth Consolidated, 13½ million. Other major sources of gold within this segment of the Mother Lode in Ama-

dor County have been the South Eureka, Bunker Hill, Zeila, Fremont-Gover, Wildman and Mahoney, Oneida, and Original Amador mines.

From Amador County northward nearly all of the Mother Lode veins are in Mariposa slate of Jurassic age, but south of Amador County they occur in a variety of rocks of Upper Jurassic to Paleozoic age. Such rocks include greenstone, serpentine, and mica schist. Along some segments of the southern part of the Mother Lode the veins have formed at or close to the contact of two of these rock types. Major mines of the Mother Lode outside of Amador County include the Mariposa, Pine Tree and Josephine, Virginia, Mary Harrison and Malvina in Mariposa County; App-Heslep, Eagle-Shawmut, Harvard, Jumper and Rawhide in Tuolumne County; the mines at Carson Hill, and the Utica and Gold Cliff at Angels Camp, all in Calaveras County; and the Union, Pacific, Sliger and Black Oak in El Dorado County. The Carson Hill mines have a total output valued at 26 million dollars, and the Utica mine production is valued at 17 million dollars.

In the Sierran foothills, all mines east of the Mother Lode have been grouped under the name "East Belt". East Belt veins cut a variety of rocks—metasediments, greenstone and granodiorite—and the veins have no well-defined preferred orientation. In general the East Belt veins are narrower and the ore shoots smaller than those of the Mother Lode, but the ore shoots commonly are richer. Many of them have averaged \$50 or more per ton in gold. The ores are more complex than in most Mother Lode mines and commonly contain appreciable amounts of chalcopyrite, arsenopyrite, galena and sphalerite in addition to pyrite. The most productive East Belt mines have been the Sheep Ranch mine, Calaveras County; the Mount Pleasant and currently active Hazel Creek mines near Grizzly Flats, El Dorado County; the Confidence mine near Twain Harte and the Soulsby and Black Oak mines near Soulsbyville, Tuolumne County;

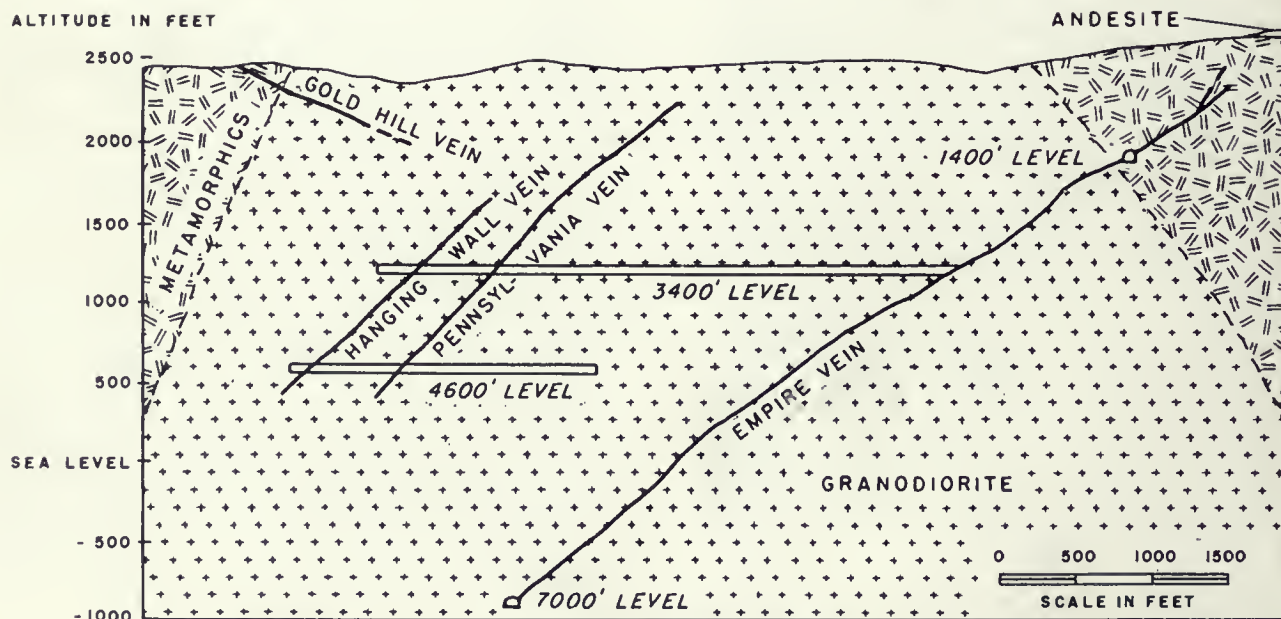


FIGURE 2. Generalized section through the Pennsylvania mine, Grass Valley. (After Johnston, 1940, p. 86.)



and the Clearinghouse, Hite and Hasloe mines in Mariposa County.

Gold-bearing veins of the Sierran foothills west of the Mother Lode have been referred to by some workers as the "West Belt" deposits. Some of the veins occur in metamorphic rocks near contacts with granitic intrusive bodies, whereas others cut metamorphic rocks but seemingly are unrelated to such contacts. Still others are associated with a variety of igneous dike rocks. The gold in the West Belt deposits, like some of the gold in the Mother Lode, occurs with pyrite in altered metamorphic rock adjacent to veins as well as in the quartz veins themselves. The leading West Belt mines have been the Zantgraf, south of Auburn, the Big Canyon and Pyramid mines near Shingle Springs, all in El Dorado County; the Gold Knoll, Mountain King and Royal mines of the Copperopolis district, Calaveras County; and the Mount Gaines and Washington mines of the Hornitos district of Mariposa County. Gold is also an important constituent in ores of the foothill copper-zinc belt (see copper section of this bulletin).

Substantial amounts of gold were mined in the Ophir district just west of Auburn, Placer County, where gold-quartz veins are associated with a granodiorite intrusion. At Colfax, in Placer County, is another notable gold-mining district. Here the Rising Sun was the principal mine. Further east near Dutch Flat, the Pioneer mine was a major source of gold.

The Grass Valley-Nevada City district of Nevada County, lying 50 miles north to northwest of the Mother Lode, contains the two largest and most productive lode-gold mines in California as well as many other major gold mines. Gold-quartz veins in this area occupy complex fracture zones in granodiorite and metamorphic rocks of Paleozoic and Jurassic age.

At Grass Valley, the veins occur in two main systems and are associated with an elongate north-trending granodiorite body. The veins in one system trend northerly and dip gently, some eastward and some westward. These occur in granodiorite or metamorphic rocks adjacent to the granodiorite. The veins of the other system trend west or northwest, dip both northward and southward, and are in metamorphic rocks, some just to the south of an extensive serpentine mass northeast of Grass Valley. Many of the productive veins of both systems extend into granodiorite at depth. The veins vary widely in lateral extent, and most of them are 10 feet or less in thickness (Johnston, 1940, p. 31). Gold occurs in the quartz and in sulfides, principally pyrite within the veins. The veins also contain smaller amounts of galena, sphalerite, arsenopyrite, chalcopyrite, and minor amounts of scheelite. Rich "high-grade" pockets occasionally are encountered in the veins. The ore shoots show a great range in size, and many have irregular shapes. The Empire vein has been worked to an inclined depth of more than 11,000 feet.

The largest mining operation of the Grass Valley district has been that of the Empire-Star Mines Company, Ltd. This mine is a consolidation of the Empire, North Star, and Pennsylvania mines and has a total gold output valued at more than \$130,000,000. The total output of the Brunswick and Idaho mines of the Idaho-Maryland Mines Corporation is valued at more than \$60,000,000. Other properties at Grass Valley that have yielded

large amounts of gold include the Golden Center, Union Hill, Allison Ranch, Golden Gate, and Norambagua mines.

In the Nevada City district about 5 miles east of Grass Valley, gold-bearing quartz veins occur where metamorphic rocks have been intruded by granodiorite. The best-known mine is the Lava Cap, which yielded \$12,000,000 in less than ten years. The other principal lode mines were the Murchie, Champion, Pittsburgh, Mountaineer, and Providence.

At Washington, 14 miles northeast of Nevada City, gold-bearing quartz veins occur in metamorphic rocks and granite. In this area, the Yuba and Gaston mines have been the principal sources of gold. East of Washington, and also in Nevada County, is a belt of gold-bearing veins in granite and metamorphic rocks extending from Graniteville south to Emigrant Gap. The Zeibright mine north of Emigrant Gap was a large recent operation. Substantial amounts of lode gold also have been produced at French Corral northwest of Grass Valley, at North Columbia north of Nevada City, at Rough-and-Ready west of Grass Valley, and near Meadow Lake in eastern Nevada County.

The Alleghany-Downieville district of Sierra County, 25 miles northeast of Grass Valley, is famous for the richness of its gold mines. Here, quartz veins fill reverse faults in metamorphic rocks of Paleozoic age. The gold occurs in the quartz and in relatively small but rich pockets, some of which assay \$2000 per ton or more in free gold (Ferguson and Gannett, 1932, p. 52). Only small amounts of sulfides, principally arsenopyrite, are present. The presence of numerous bodies of serpentine has had a profound influence on the localization of ore shoots. Individual shoots have yielded from a few hundred to hundreds of thousands of dollars worth of gold. The Original Sixteen-to-One mine, which has had a total output of over \$16,000,000, has been the largest source of gold in the district. Other notable mines are the Brush Creek, Oriental, Plumbago, Rainbow, and Kate Hardy.

Fifteen miles east of Downieville is the Sierra Buttes district where gold-quartz veins occur in metasedimentary and metavolcanic rocks of Paleozoic and Jurassic age. The Sierra Buttes mines, which had a total output of about \$17,000,000, and the Young America, Mountain, and Phoenix mines have been the chief sources of gold. In the Pike district in southwestern Sierra County, gold-quartz veins are in metavolcanic rock. The Alaska mine was the largest operation.

Gold has been produced from several areas in eastern and northeastern Yuba County, particularly the Browns Valley, Brownsville, and Smartsville areas. Quartz veins, some of which have yielded rich pockets, are in metamorphic rocks near granite.

In eastern Butte County, gold-bearing quartz veins occur in metavolcanic rock near extensive bodies of granodiorite. These deposits have been developed principally by the Gold Bank mine near Forbestown, the Matheson mine near Magalia, and the Surcease mine north of Oroville. In Plumas County, large amounts of lode gold have been mined in the Johnsville district where gold-quartz veins occur in metasediments of Paleozoic age that have been intruded by gabbro and diorite. Here, the principal operations have been the Plumas-Eureka and Jamison mines. Near Crescent Mills, where



substantial amounts of gold were produced from gold-quartz veins in granodiorite, the Green Mountain and Indian Valley mines were the chief sources of gold.

*Placer Deposits of the Western Sierra Nevada.* The alluvial or placer gold deposits of the western Sierra Nevada have contributed more than 40 percent of California's total gold output. They have been formed by the erosion of pre-existing veins and are divisible into early Tertiary (older) deposits and the Quaternary (younger) deposits.

The early Tertiary placers consist chiefly of quartz gravel. In 1911, they were estimated to have yielded about \$300,000,000 in gold (Lindgren, 1911, p. 81). The early Tertiary gravels were buried by later Tertiary lavas, and new systems of streams developed. Most of the channel deposits that formed during the later Tertiary volcanic episode are lean in gold. When the Sierras were re-elevated, the new streams cut through the older surface, but in many areas the thick volcanic cover preserved the early Tertiary channels. Most of the output of Tertiary placer gold has been obtained by hydraulic mining, but some deposits were extensively worked by underground mining. Such mines are known as drift mines.

The most productive Tertiary channel deposits have been as follows: (1) The Magalia channel near Magalia, northeastern Butte County, which is of limited extent, and in which drift mines such as the Emma, Indian Springs, and Perschbaker have been the most productive; (2) The channel at Table Mountain north of Oroville which has been developed by the Cherokee hydraulic mine with a total output of more than \$13,000,000; (3) The various branches of the Tertiary Yuba River, in Plumas, Sierra, Nevada, and Yuba Counties, which have yielded enormous quantities of gold by hydraulic and drift mining, particularly in the La Porte district of Plumas County, which has a total output of more than \$60,000,000, the Gibsonville, Brandy City, Downieville, and Alleghany areas of Sierra County, the Camp-tonville area in Yuba County, and the Washington, North Bloomfield, North Columbia, North San Juan, Lowell Hill, and French Corral areas in Nevada County; (4) Branches of the Tertiary American River in Placer and El Dorado Counties where highly productive mines have existed in the Dutch Flat, Gold Run, Yankee Jims, Iowa Hill, Foresthill, Michigan Bluff, Last Chance and Placerville-Diamond Springs districts; (5) Branches of the Tertiary Mokelumne River of which the richest portions were at Indian Diggings, El Dorado County; and Fiddletown, and Volcano, Amador County; (6) Tertiary Calaveras River, in Calaveras County where productive drift mines have been worked on channels at Mokelumne Hill, Vallecito, and Altaville, and where considerable hydraulic mining was done at Douglas Flat; and (7) Tertiary Tuolumne River in Tuolumne County which contains some of the richest placers in the Sierra Nevada, especially the Columbia district whose total gold output is valued at about \$87,000,000.

In the Quaternary period another group of streams was established and developed into the present river systems. These swept away much of the Tertiary volcanic cover, completely removed long sections of the earlier rivers, and cut new canyons in the bedrock.

Some of these canyons are 2,000 to 2,500 feet below the old surface. This tremendous amount of erosion caused large quantities of gold to accumulate in the main streams and their branches. These Quaternary deposits range in size from the small but rich placers only a few square feet in extent which were worked during the early days of the gold rush, to the large but low-grade deposits covering many square miles and which have been worked by modern bucket-line dredges. Some of the rich surface placers, worked during the early days, contained many dollars worth of gold in a cubic yard. The deposits in the dredging fields commonly contain 25 cents or less per cubic yard, but vast amounts of gold-bearing material are dredged. Individual dredges treat as much as 5 million cubic yards of gravel per year.

Quaternary placer deposits have been dredged extensively along the Feather River near Oroville, Butte County; the Yuba River near Hammonton, Yuba County; the American River near Folsom, Sacramento County; the Mokelumne River in eastern San Joaquin and western Calaveras Counties; the Tuolumne River near La Grange, Stanislaus County; and the Merced River near Snelling, Merced County.

Residual placers, those in which gold has been released from the enclosing rock but not transported from the original site are common in and near the Mother Lode belt in northern El Dorado County. Locally they are called "seam diggings". The most productive seam mines were at Georgia Slide a few miles north of Georgetown.

*Other Gold-Bearing Regions.* Apart from the west slope of the Sierra Nevada, gold also occurs in a number of areas along the east flank of the central and north parts of the range. In the Diamond Mountain district, a few miles south of Susanville, Lassen County, gold has been produced from quartz veins in granitic rocks and from stream gravels. It also was produced as a by-product from large copper mines to the south in Plumas County. Gold also was produced from the Mogul and Monitor districts southeast of Markleeville in Alpine County. Here large but low-grade gold-bearing silicified zones cut andesite.

West of Mono Lake, Mono County, is the Lundy district where gold-bearing quartz veins are in slate and granite. The May Lundy mine was the chief source of gold in this district. In western Inyo County, gold has been produced from several districts on the east flank of the Sierra Nevada. These include the Bishop Creek area southwest of Bishop, in which the Wilshire-Bishop mine is the most noteworthy, and the area west of Kearsarge. Small amounts of gold are produced as a by-product of tungsten mining in this region.

Large quantities of gold have been produced from the Klamath Mountains in the northwestern part of the state, principally from Shasta, Siskiyou, and Trinity Counties. In this region gold-bearing quartz veins occur in metamorphic rocks of Paleozoic age that have been invaded by granitic rocks of Jurassic age. Many dikes are associated with the gold veins. Gold also occurs in the massive sulfide bodies of the Shasta copper-zinc belt north of Redding, and in placer deposits which have been worked extensively.

In the Klamath Mountains, the most productive area for lode gold was the Deadwood-French Gulch district of Shasta and Trinity Counties. Notable gold mines in



this district included the Brown Bear, which has a total output of more than \$8,000,000, and the Gladstone, Milkmaid, and Washington mines. Other formerly productive districts in Shasta County are at Harrison Gulch, where the Midas mine was a major source of gold; the Old Diggings district, where the Reid and Walker mines were extensively operated; and the Whiskeytown district where the Mad Mule was important. Much gold also was mined in the Cecilville-Black Bear district of Siskiyou County, where the King Solomon mine was a noted operation. Other highly productive gold mines in the region include the presently active Siskon mine near Happy Camp, Siskiyou County; the Golden Eagle north of Fort Jones, Siskiyou County; the Uncle Sam near Kennett, Shasta County; the Bully Choop south of Douglas City, Trinity County; and the Globe area near the town of Dedrick, Trinity County.

In the Klamath Mountain region also, large quantities of placer gold have been produced by dredging and hydraulic mining, particularly during the 1930's. Extensive deposits of gold-bearing gravels are in and along the Klamath, Scott, Trinity, Salmon, and upper Sacramento Rivers as well as a number of large creeks. Not only is gold found in the stream beds themselves, but also in terrace and bench deposits on the sides of the present river channels. These terrace deposits range from Pleistocene to Recent in age. In recent years large dredging operations have been active on branches of the Trinity River at Trinity Center, Lewiston, Hayfork, and Junction City; on the Salmon River near Sawyers Bar; on the Klamath River near Seiad, Yreka, and Horse Creek; on Clear Creek near French Gulch; on the Scott River near Callahan; along Cottonwood Creek; on the Sacramento River south of Redding; and in the Igo district west of Redding. Hydraulic mining also has been very extensive, particularly in the Weaverville and Coffee Creek areas.

In Modoc County, of northeastern California, gold has been produced from the High Grade district in the Warner Mountains and the Winters district southwest of Alturas. Shallow gold-bearing veins occur in fault zones in volcanic rocks of Tertiary age. Appreciable amounts of gold were mined in the Hayden Hill district in northern Lassen County. Here, gold associated with manganese is found in brecciated zones in Tertiary volcanic rocks. The largest sources of gold in this district were the Golden Eagle, Juniper, and Brush Hill mines.

East of the Sierra Nevada, in Mono and Inyo Counties, are a number of famous gold mining districts. More than \$30,000,000 worth of gold has been produced at Bodie in eastern Mono County, where gold-bearing quartz veins are in andesite. The largest gold mine in the area is the Standard, which has had a total output of more than \$18,000,000. Other well-known sources of gold of the Bodie area were the Southern Consolidated and Syndicate mines. In the Masonic district, north of Bodie, gold occurs in quartz veins in metamorphic rocks and granite. Here, the Pittsburgh-Liberty mine was the largest operation.

In the Inyo Range northeast of Lone Pine is the Russ district where gold-bearing quartz veins are in Paleozoic metamorphic rocks intruded by granite. Here, the Brown Monster-Reward mine was a noted producer. The Keane Wonder mine in the Funeral Range north of Death Valley also was a major source of gold. In the Wildrose district

of the Panamint Range, gold-bearing quartz veins occur in quartz monzonite. Here, the Skidoo mine was the principal operation. East of Ballarat, and on the west side of the Panamint Range is the Ratcliff gold mine, which was highly productive. In this area gold-quartz veins are in schist. Gold is a minor but economically important constituent of the lead-silver and copper deposits in Inyo County.

Kern and San Bernardino Counties contain the largest gold mines in southern California. The Randsburg district, which lies athwart the mutual line of the counties and which has been especially productive, contains gold and silver-gold mineralization in quartz veins and as impregnations and stockworks in quartz monzonite of Mesozoic age and in pre-Cambrian schist. The Yellow Aster, which has a total output of more than \$12,000,000, was the largest mine. Other mines of the district, which were highly productive were the Black Hawk, California Rand Silver, and Sunshine. Substantial amounts of placer gold have been recovered in the Goler Gulch area of the El Paso Mountains.

In the Mojave-Rosamond district of southeastern Kern County, gold-quartz veins occur in or near rhyolite plugs that are intrusive into quartz monzonite. The most productive mines in the area have been the Cactus Queen, Exposed Treasure and Desert Queen, Golden Queen group, and Tropico mines. At the Cove district, which lies in the part of the Sierra Nevada that extends into northeastern Kern County and which is near the town of Kernville, gold-bearing quartz veins are associated with Paleozoic schist and Jurassic granitic rock. The most productive mines of this area were the Big Blue and Sumner group. Other large gold mines of Kern County include the Joe Walker, Saint John, and Amalie mines east of Bakersfield in the Sierra Nevada.

Significant amounts of gold have been mined throughout San Bernardino County, but the principal source has been the Bagdad-Chase mine south of Ludlow, where gold and copper deposits are found along contacts between bodies of quartz monzonite and rhyolite. In the Dale district southeast of the town of Twenty-Nine Palms, gold-quartz veins occur in andesite porphyry. The chief mines of the Dale district were the Supply and Nightingale. Gold also has been produced in the Whipple Mountains, the Ivanpah Range, the New York Mountains, and the Old Woman Mountains.

Gold occurs in numerous areas in Riverside, Imperial, and San Diego Counties. Most of the gold mined in Riverside County has been obtained from the Pinacate district, where there are gold-quartz veins in granodiorite. The principal operation in this district was the Good Hope mine.

Substantial quantities of gold have been produced from quartz veins in pre-Cambrian (?) schist and gneiss in the Cargo Muchacho and Picacho Mountains of southeastern Imperial County. The chief gold operation of the Cargo Muchacho area were the American Girl and Golden Queen mines, whereas the Picacho mine had the greatest output of those in the Picacho district. Substantial amounts of placer gold also were produced from the Picacho area as well as from the Potholes area near the Laguna Dam, which is east of the Cargo Muchacho Mountains. Gold also has been produced from the Paymaster silver district in the Chocolate Mountains.



## GENERALIZED GOLD MILL CIRCUITS

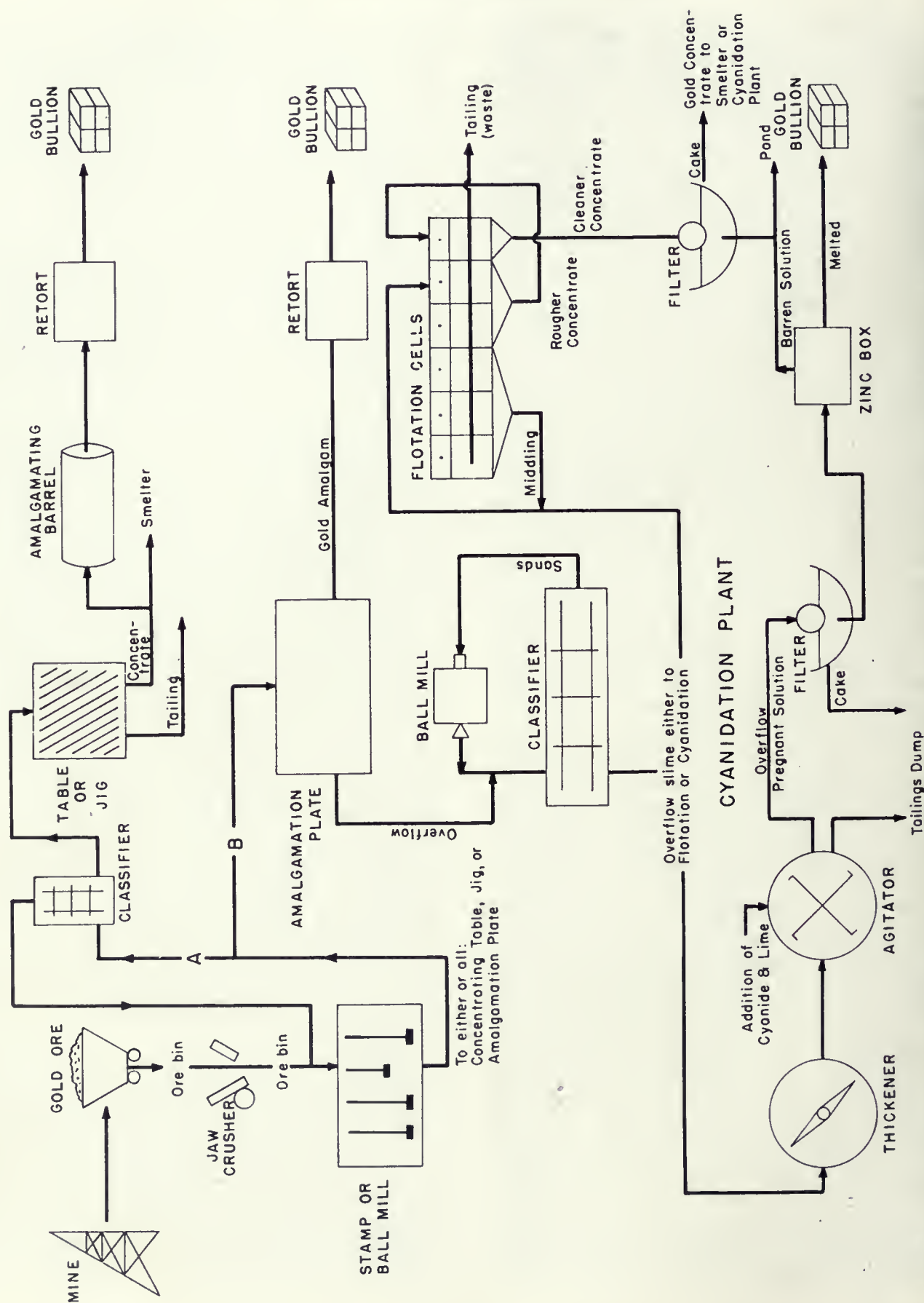


FIGURE 3. The progressive treatment of gold ore as it "flows" from the mine through the mill shown diagrammatically. A simple treatment is indicated by Circuit A, a more complex treatment by Circuit B. Although many variations of Circuits A and B are possible, only one circuit would be used at an individual mine.



Gold has been mined in the Julian-Banner district, in the Peninsular Ranges of San Diego County, where gold-bearing quartz veins occur in Triassic schist that has been intruded by granite and granodiorite. Less extensive operations were active around Escondido and in northern San Diego County along the Riverside County boundary.

Several million dollars worth of gold has been produced from the San Gabriel Mountains of Los Angeles County, mostly from the Governor mine near Acton, where gold-quartz veins cut quartz diorite. Placer gold has been obtained from Quaternary deposits in the Saugus district and from the San Gabriel River channel. Gold also has been mined in northeastern Ventura County, notably the Frazier Mountain mine, which has developed a gold-quartz vein in schist and slate.

Gold has been found throughout the Coast Ranges, but the deposits are small, and the production has been sporadic. Small gold, silver, and copper-bearing veins as well as a few massive pyrite bodies with small amounts of gold occur in metamorphic rocks of the Franciscan group and granitic rock. Small amounts of gold also have been recovered in black sands and in beach and stream deposits tributary to the Coast Ranges. The principal source of gold in the Coast Ranges has been in the Los Burros district in southwestern Monterey County.

**Utilization.** The chief function of gold in the United States is as a foundation upon which to base the monetary system, and its use is closely regulated. Prior to 1934, gold coins circulated freely in the United States and to a lesser extent in other countries. It has continued to serve in the settlement of international debts and in this sense is still considered as international money. On December 31, 1954, the United States had an official gold reserve of \$21,712,306,402, nearly all of it in the form of bullion.

Large quantities of gold are used in the arts. The widespread prosperity that has followed World War II and high marriage rate have increased the demand for jewelry, watches, gold leaf, and many luxury items made of gold. The properties of gold such as resistance to corrosion and its malleability make it useful in dentistry and industry. It is used in gilding and plating, in chemical and laboratory ware, and as an alloy in thermo-electrical instruments. In medicine, radioactive gold salts are used in the treatment of certain diseases.

**Markets.** Since 1934, when gold was withdrawn from circulation in the United States, the only gold that can be legally acquired, transported in the country, imported, or held in custody for domestic account without a license is gold in its natural state. This is defined by the U. S. Treasury as gold "recovered from natural sources which has not been melted, smelted, or refined or otherwise treated by heating or by chemical processes." \* Persons in California engaging in purchasing gold ores, concentrates, or amalgams are required by law to have a state license. \*\* Such licenses are issued by the State Division of Mines. All newly mined gold not in its natural state must be sold either to the U. S. Mint or to a

licensed buyer. The price paid by the U. S. Treasury for gold purchased by the mints is \$35 per troy ounce of fine gold, less  $\frac{1}{4}$  of 1%; 85 $\frac{1}{4}$  cents per fine ounce is paid for the contained silver. Gold for industrial uses is sold to licensed buyers by the government.

Because of the unsettled condition of many foreign currencies, gold has been in demand in parts of Europe, Asia, and Africa at prices higher than the official price of \$35 per ounce. However, producers in the United States are prevented by law from shipping gold to these markets.

**Mining and Milling Methods.** Small and generally crude tools were used to recover gold from placers during the early days of the gold rush in California. Extensively employed were the miner's pan and its wooden version, the batea, which was introduced by Mexicans. Devices, such as sluice boxes and rockers or cradles were introduced later; these increased the amount of material that each miner could handle and the percentage of gold recovered.

Hydraulic mining, a still later development, consists of directing large jets of water against the banks of gold-bearing gravel which commonly are several hundred feet high. Gold is recovered partly by cleaning bedrock after the gravel has been stripped away and partly in riffles in the string of sluice boxes through which the washed gravels and water flow. In drift mining, pay streaks in the old river channels are developed by drifts and cross-cuts. The excavated gravels are sluiced or sent through a washing plant to recover the gold.

Floating bucket-line dredges, now the principal means of placer gold recovery in the state, handle large amounts of gold-bearing gravels with a small crew. The gravels excavated by the buckets are sent through a trommel or revolving screen which discharges the oversize gravels. These are then stacked in large piles by conveyor belts. Undersize material from the trommel is delivered to gold-saving tables equipped with riffles, to jigs, or to a combination of both, where the gold is recovered. Dragline dredges or "doodlebugs" combine a dragline and a floating or dry-land washing plant equipped with a trommel and banks of riffles.

Virtually all of the operations on lode gold deposits in California are underground mines. Square-set stopes are the most common in California's gold mines, although shrinkage stopes are locally employed. Sand- or waste-filling is employed in some of the larger mines. Wherever possible, mechanical devices, such as loaders, scrapers, and locomotives, are used underground to lower mining costs. Considerable amounts of water are encountered in most California gold mines. Consequently much pumping equipment is used.

Lode-gold ores are treated by several processes each of which involves crushing and fine grinding as preliminary steps. Ball mills or stamp mills usually are employed in fine grinding. The gold is recovered from the finely ground ore by amalgamation, flotation, jigging, table concentration, or a combination of these processes (fig. 3). In amalgamation, gold-bearing material is brought into contact with mercury, and an amalgam of gold and mercury is formed. The gold is then recovered by distilling off the mercury. In a jig, the gold is agitated in water and separated from lighter material by a vertical pulsating motion, whereas concentrating tables

\* U. S. Treasury Department provisional regulations issued under the Gold Reserve Act of 1934, Art. 2, Sec. 19, January 30 and 31, 1934.

\*\* Public Resources Code of the State of California, Division II, Chapter 3, and amendments. -



**American Smelting and Refining Company**  
**SELBY SMELTING WORKS**  
**Selby, California**

**PURCHASE SCHEDULE****DATE EFFECTIVE:** January 31, 1956

<b>Shipper</b>	<b>Address</b>
<b>Mine</b>	<b>Location</b>
<b>Character Ore</b>	<b>R. R. Station</b>

GOLD - SILVER

ORES AND CONCENTRATES

The following purchase terms are subject to the General Clauses shown on the back of this sheet, and are subject to prompt acceptance. Unless shipments are begun within 30 days this quotation is automatically cancelled.

**TONNAGE:** Limited to 100 tons per month except by special arrangement.

**DELIVERY:** F.O.B. unloading bins American Smelting and Refining Company, Selby, California.

**PAYMENTS**

**GOLD:** If .03 of a troy ounce per dry ton or over and less than 5.00 ounces, pay for 91.14%; if 5.00 ounces per dry ton or over and less than 10.00 ounces, pay for 92.57%; if 10.00 ounces per dry ton or over and less than 15.00 ounces, pay for 93.28%; and if 15.00 ounces per dry ton or over pay for 94.0% at the net price per ounce paid by the United States Mints for gold recovered from domestic mine production on the 15th day following the date of delivery of product at Buyer's Plant. Nothing paid for gold if assaying less than .03 of a troy ounce per dry ton.

**SILVER:** Pay for 95% at the average Handy & Harman New York silver quotations for the calendar week including date of delivery of the last car of each lot at plant of Buyer or at the realized Mint price if higher, provided silver qualifies for Government purchase and affidavit is furnished. In case Handy & Harman shall discontinue publishing quotations for silver then the New York quotations for silver as published by the Engineering and Mining Journal shall govern. Minimum deduction one Troy ounce per dry ton.

No payment will be made for any metal or content except as above specified.

**DEDUCTIONS**

**BASE** \$ 8.50 per net dry ton of 2,000 pounds; provided the sum of payments for gold, silver  
**CHARGE:** does not exceed \$ 20.00 per ton. Add to the base charge 10 percent of the excess over  
 \$ 20.00 to a maximum charge of \$ 15.00 per dry ton.

**INSOLUBLE:** Allow all units free; charge for excess at cents per unit, fractions in proportion.

**ARSENIC, ANTIMONY**

**AND TIN COMBINED:** 1% free. Excess charged at 50c per unit, fractions in proportion.

**ZINC:** 7% free. Excess charged at 30c per unit, fractions in proportion.

**BISMUTH:** Charge for all at 50c per pound, fractions in proportion.

**MOISTURE:** A minimum deduction of 1% will be made from wet weight; when over 1% contained, actual moisture will be deducted. Moisture in excess of 10% will be charged at 10c per unit, fractions in proportion.

**TAXES:** See Clause 1 on reverse side of this schedule.

**SHIPMENT:** The rates quoted are based upon shipment in solid or flat dump bottom gondola equipment. Extra unloading charge of 75c per dry ton will be assessed for products received in box cars or hopper bottom gondolas, and actual cost of unloading products received by truck.

**FREIGHT:** All railroad freight and delivery charges for account of shipper. Deduct from settlement, freight and other advances made by Buyer.

CONSIGN ALL SHIPMENTS TO THE AMERICAN SMELTING AND REFINING COMPANY, SELBY, CALIFORNIA, AND MAIL ORIGINAL BILL OF LADING AND LETTERS WITH INSTRUCTIONS FOR MAKING PAYMENT TO OUR SAN FRANCISCO OFFICE, 405 MONTGOMERY STREET.

**AMERICAN SMELTING AND REFINING COMPANY**

FIGURE 4. Gold and silver ores and concentrates purchase schedule of the American Smelting and Refining Company, Selby smelter. Courtesy American Smelting and Refining Company.



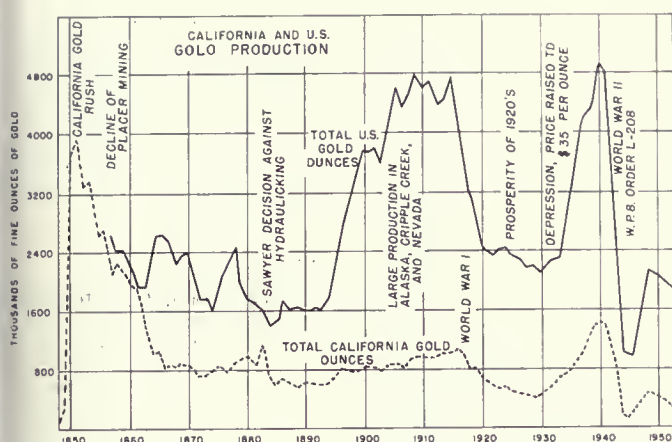


FIGURE 5. Chart showing production of gold in California, 1848-1953, and total United States production, 1857-1953.

recover gold by a horizontal shaking motion. In some of the larger mills, the concentrate and tailing or the tailing alone are treated by cyanidation. In this process, sodium cyanide solution is added to gold-bearing materials and the gold is dissolved. It then is recovered from the solution by precipitation.

Concentrates usually are shipped to a smelter. The smelter nearest to most gold mines in California is that of the American Smelting and Refining Company at Selby, although gold ores and concentrates have been shipped to other smelters in Arizona and Utah. The Selby smelter purchases gravity and flotation concentrates as well as impure dredge gold, cyanide precipitates, scrap gold, and some high-grade ore. An open purchase schedule for gold and silver ores and concentrates of the Selby smelter effective January 31, 1956 is reproduced in figure 4. This schedule is subject to change without notice, so potential shippers should check with the smelter before shipment is made. A few of the larger mines purchase ores and concentrates from other mines. This procedure has been very helpful to the operators of small mines in the area, as it saves them the trouble and expense of erecting a mill for the treatment of small lots of ore or the expense of shipping ore great distances to a smelter.

A person who wishes to put into production an inactive gold mine or an undeveloped gold deposit is faced with a difficult problem, as the price of gold is the same as before World War II while labor and material costs have increased greatly. Consequently most gold deposits mined profitably during the 1930's and early 1940's are now non-commercial. The reopening of many mines is further deterred by the high cost of rehabilitating and dewatering. Moreover, the small operator, who wishes to make use of a nearby mill, either on a custom basis or by selling his ore to the operator of such a mill, now has at his disposal a much smaller number of mills than before World War II. The few mills now active in California are largely in the Grass Valley, Alleghany, and East Belt areas of the Sierra Nevada.

**History of Production.** As early as 1775, small amounts of placer gold were produced by Mexicans from the area around the Colorado River and from lode deposits in the Cargo Muchacho Mountains. In 1828, gold was discovered at San Isidro, San Diego County. For a

period of about 20 years following 1838, placer gold was produced in the Newhall area of Los Angeles County.

Gold mining did not become a major industry in the state until after James W. Marshall's discovery at Coloma on the American River in 1848. The large output of gold from the rich virgin placers during the following few years had a profound effect on the United States and on the development of California. In 1852, these deposits yielded more than \$81,000,000 worth of gold, which was more than 60 percent of the world production for that year (Joslin, 1945, p. 122). Although the annual production declined to less than \$20,000,000 in the late 1860's, gold continued to be the state's leading metal.

Hydraulic mining, introduced in 1852, yielded most of California's gold production from the late 1860's until 1884 when a court decree, known as the Sawyer decision, severely curtailed hydraulic mining by prohibiting the dumping of debris in the Sacramento-San Joaquin River systems. In the 1880's and 1890's, extensive drift mining of buried auriferous channels partly compensated for the loss of placer gold production by hydraulic mining.

Lode mining in California began on a small scale about 1850 and became widespread in the late 1860's. Many of the major improvements in mining and milling methods were originally developed in these early mines. Stamp mills replaced the arrastre. Concentrating devices such as vanners and tables and the cyanidation process were introduced which lowered milling costs and increased recovery. Thus material formerly discarded as waste could be considered ore. From 1884 to 1918, lode mines were the chief source of gold in California.

Floating bucket-line dredges, which were introduced in California from New Zealand in 1898, became highly productive and continue to be so. They are now the principal source of placer gold in California. Dragline dredges and washing plants were important sources of gold in the 1930's.

The gold production curve for California shows a series of fluctuations (fig. 5). "Boom" periods are always unfavorable for gold mining as labor and materials become expensive, but, as the price generally remains fixed, the higher operating costs cannot be covered. From a negligible production in 1848, the output from the rich virgin surface placers jumped in value to over \$81,000,000 in 1852, an all time high. These were rapidly depleted, and by 1865, annual production had fallen to \$17,000,000, and production leveled off until 1873 when the demonetization of silver caused another drop. The Sawyer decision against hydraulic mining caused production to decrease again after 1884, but it gradually rose during the period 1900 to 1918 when gold dredging became widespread. During World War I and the prosperity of the 1920's, rising costs caused another decline.

During the depression that began in 1929, gold production increased, first slowly, and then sharply when gold was revalued from \$20.67 to \$35 an ounce. In 1939, and again in 1940, the total annual production exceeded \$50,000,000, the highest figures since 1856. At the beginning of World War II, gold production fell because of high wages and scarcity of materials. Further restrictions by the promulgation of War Production Board



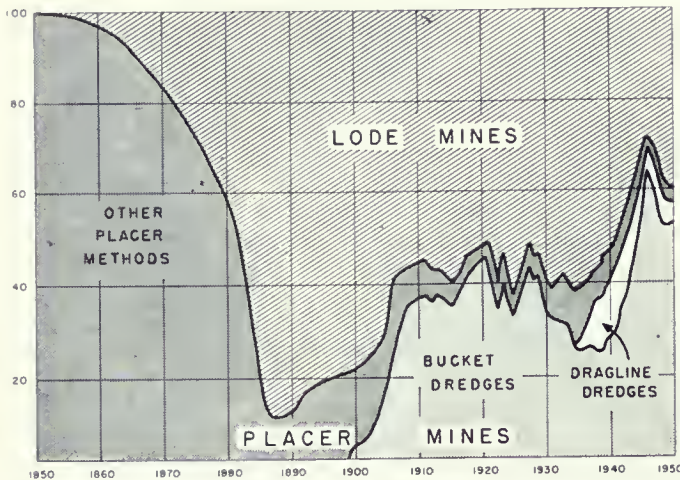


FIGURE 6. Percentage of total California gold produced at lode and placer mines and by various methods of placer mining 1850-1950. (After U. S. Bureau of Mines Minerals Yearbook, 1950, p. 1419.)

Order L-208 on October 8, 1942, caused production to drop to less than \$5,000,000 in 1944.

The order was lifted on July 1, 1945, and gold production rose. Gold dredging was resumed on a scale nearly equal to that before the war. However, many of the important lode mines remained closed.

From 1947 to 1953 gold production in California followed a diminishing trend. However, since 1953, it has increased slightly. The estimated output for 1955 is 250,000 troy ounces valued at \$8,767,500. In 1954, the output was 237,886 troy ounces valued at \$8,326,010. Yuba County ranked first in 1954 with an output of \$2,378,460. This production was largely from the Yuba Consolidated Gold Fields' bucket-line dredges in the Yuba River district near Hammonton. The five dredges of the Natomas Company south of Folsom contributed most of the output of \$2,165,310 in Sacramento County, the second most productive county in 1954. Nevada County ranked third with a production of \$1,985,060. Much of this production was from the two large lode mines at Grass Valley, the Empire Star group owned by Empire Star Mines, Ltd. and the Brunswick mine owned by the Idaho-Maryland Mines Corporation. Siskiyou County was fourth in 1954 with an output of \$488,985, the Siskon mine near Happy Camp being a major source of gold. Sierra County, which was in fifth place, had an

output of \$468,405. This was largely from lode mines in the Downieville-Alleghany area, especially the Original sixteen to one and Brush Creek mines.

Other sources of gold in 1954 included lode mines in Calaveras, El Dorado, and Kern Counties, a bucket-line dredge in Trinity County, and by-product gold from base metal and tungsten ores in Amador, Calaveras, Inyo, and San Bernardino Counties.

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FIGURE 7. Old Eureka shaft, Central Eureka gold mine on the Mother Lode, Sutter Creek, Amador County. This mine has a total gold output valued at more than 36 million dollars. It was worked to an inclined depth of 4200 feet. Photo by T. Calvert Slater.



FIGURE 8. Natomas Company gold dredge, American River district near Folsom, Sacramento County, California. The dredge pictured above treats several million cubic yards of gold-bearing gravel each year.









FIGURE 10. One of the badland areas just south of sugarloaf, part of the Cherokee hydraulic mine. The white gravel so well exposed in this photograph was rather poor in gold. Pay streaks were few and most of the quartz gravel contained only a few cents per yard of gold. Much of the gold is reported to have come from iron-oxide-cemented crusts at the base of and scattered within the white gravel section. *Photo by Mort D. Turner.*

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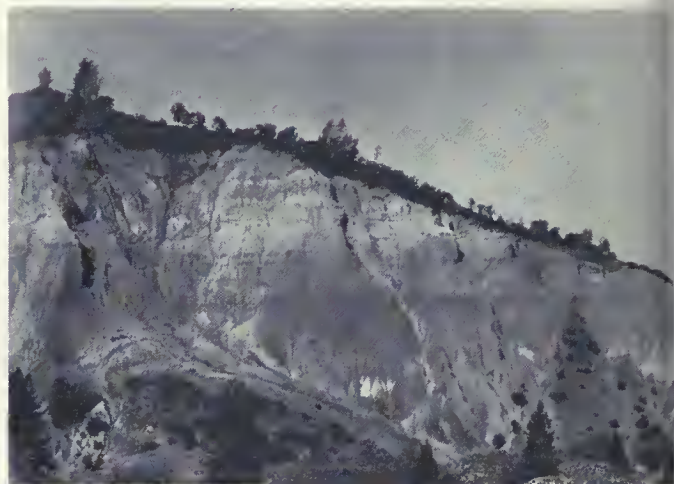


FIGURE 11. A typical face in the Cherokee hydraulic mine at Cherokee, Butte County, camera facing west across Sawmill Ravine. Piles of greenstone gravel tailings from the lowermost channel deposits are piled in the foreground. Most of the gold recovered apparently came from these gravels and only a minor amount from the 150-foot-thick section of white gravels which show through the talus cones in the right middle ground. Above the white gravel is about 200 feet of red kaolinite clay and the sediments are capped by 150-200 feet of basalt. *Photo by Mort D. Turner.*

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## GRAPHITE

BY GORDON B. OAKESHOTT

Graphite is widely distributed in pre-Cretaceous metamorphic rocks throughout California, but the owners of graphite deposits in the state have had difficulty in meeting competition provided by the higher quality imported material. From 1865 to 1935, graphite was produced spasmodically, chiefly from Tuolumne, Sonoma, and Los Angeles Counties, but no production has been recorded since. The total yield of these deposits is estimated to be about 1,500 tons, valued at \$137,000. Graphite consumed in California is mostly the amorphous variety, obtained mainly from Mexico; the crystalline flake variety used is largely imported from Madagascar.

*Mineralogy and Geologic Occurrence.* The mineral graphite, also called plumbago, is a crystalline form of pure carbon and is characterized by softness, perfect basal cleavage, and greasy feel. A commercial distinction made between "amorphous" and "crystalline" graphite is based solely on relative grain size; the "amorphous" variety is the finer grained. The grades and specifications of graphite used in industry are complex and involved. Particles of crystalline flake graphite may be as large as 8-mesh; particles of artificial graphite in colloidal dispersions may be only 5 millionths of an inch in diameter.

Much graphite has been formed by the metamorphism of carbonaceous sediments, including coal, with resultant crystallization of the carbon. Such graphite occurs in schists and gneisses of sedimentary origin. However, some is associated with intrusive igneous rocks, and with pegmatites; these occurrences strongly suggest an igneous origin. The mineral is also a constituent of meteorites.

Graphite occurs in nearly every country in the world but most of the graphite consumed in the United States has come from Ceylon, Madagascar, Mexico, and Canada. Ceylon amorphous graphite occurs in veins, from a fraction of an inch to several feet in thickness, which were formed along fracture planes in crystalline rocks. Mining has been by underground methods. The crystalline flake graphite of Madagascar is disseminated in metamorphic rocks which carry 5 to 10 percent graphite. Formerly mined by hand methods, it is now produced from open pits using modern earthmoving equipment obtained from the United States. The only active (1955) mining and milling operation in North America producing crystalline flake graphite is at Burnet, Texas, in the Llano Uplift area. There the graphite occurs as fine flakes in pre-Cambrian schist. It has been marketed largely for use in crucibles and foundry facings. Mexican amorphous graphite, from Sonora, occurs as beds of metamorphosed coal, as much as 24 feet thick. The high grade of ore (average 80-85 percent graphite), thickness of beds, and thickness of overburden make underground mining necessary and economic.

*Localities in California.* Graphite in California, all of the amorphous variety, occurs in schists and gneisses most, if not all, of which are of sedimentary origin. Although the graphite schists are certainly pre-Cretaceous in age, many of the age assignments given to specific occurrences are uncertain and have ranged from pre-

Cambrian to Upper Jurassic. In Los Angeles County, where graphite has been mined at several places, it occurs in crystalline limestone, quartzite, and feldspar-sillimanite-tremolite schists, all of which are metamorphosed sedimentary rocks intruded by granitic plutonic rocks. Quartz-graphite schist and other graphitic schists are common in the belt of pre-Franciscan schists south of Orick, in Humboldt County.

A third of the counties of California; chiefly in the Sierra Nevada, Klamath Mountains, Coast Ranges, and Transverse Ranges provinces, contain graphite schists which have been prospected, but the small production has come almost entirely from Tuolumne, Mendocino, Sonoma, and Los Angeles Counties.

The first graphite mined in California was probably that reported by J. Ross Browne (1868) from Tuolumne County. The Eureka plumbago mine was discovered in that county in 1853 and exported to Europe nearly all of the production of 500 tons which was mined between 1865 and 1867. Estimated value was \$100 per ton. Early operations also included one fifteen miles east of Pt. Arena, Mendocino County, and another 4 miles south of Petaluma, Sonoma County (Aubury, 1906); the latter was opened in 1894. In these two the graphite occurs in metasedimentary schist of the Jurassic (?) Franciscan group. The graphite was used in San Francisco in the manufacture of paint, as a lubricant, and in foundry facings.

In Los Angeles County several graphite schist occurrences have been worked. A deposit in the Sierra Pelona near the head of San Francisquito Creek was worked at intervals for more than 25 years prior to 1931 (Simpson, 1934). This deposit is part of the pre-Cretaceous Pelona schist. A maximum daily output of 10 tons of graphite was mined and milled. Three samples, analyzed by the United States Geological Survey, ranged from 7.29 to 17.48 percent graphite (Tucker, 1920, p. 319). The plant operated continuously from 1918 to 1920 and supplied some of the local needs for foundry facings, paint, and lubricants.

A deposit on the north slope of the Verdugo Hills,  $2\frac{1}{2}$  miles northwest of Montrose, was known as early as 1889 and graphite was mined here in 1920. This deposit and others in Los Angeles County were discussed by Beverly (1934). Deposits in upper Kagel Canyon (on the divide between Kagel and Limerock Canyons) and several in Pacoima Canyon and vicinity were described by Oakeshott (1937) who included a petrographic description of the metasedimentary graphitic schists and a geologic map of the area. The graphite in Kagel Canyon formed by metamorphism of the Placerita sedimentary formation (Paleozoic ?), remnants of which remain as crystalline limestone, quartzite and various more-or-less graphitic schists. At least two periods of metamorphism and intrusion are represented by the presence of pre-Jurassic hornblende diorite gneiss and Upper Jurassic (?) or Cretaceous (?) granite and granodiorite. A 50-ton concentration mill was constructed at the Kagel deposit and produced small-flake graphite between 1918 and 1928. The crude graphite-bearing rock contains 7



to 15 percent graphite in flakes less than 0.25 millimeter in diameter.

*Milling.* Amorphous graphite is generally ground, and coarse impurities are removed, without previous concentration. The deposits of amorphous graphite in Sonora, Mexico, are so high-grade as to make concentration unnecessary. If amorphous graphite requires concentration it is generally not worth mining. Ceylon amorphous lump graphite is concentrated by hand methods. Crystalline flake graphite, like that of Madagascar, must be concentrated to make an acceptable product. Flakes are kept as large as possible during milling as the coarser material commands a premium price. Graphite can be readily floated, but a high-grade product is difficult to obtain because, in any grinding process, graphite tends to smear grains of gangue minerals and make them floatable. Repeated cleaning is necessary to attain a high content of graphitic carbon.

*Utilization.* The most useful properties of graphite are its resistance to chemical action and the action of molten metals, its infusibility (graphite does not melt, but sublimes at about 6500° F), opacity, softness, and perfect cleavage. Its most common uses are in electrical appliances. "lead" pencils, lubricants, stove polish, paint, foundry facings, scale-preventative for boilers, mold wash for steel mills, polishes, and in powder glazing. For some of these uses both the natural material and artificial graphite made from coke are satisfactory.

A larger tonnage of graphite is used in the United States for foundry facings (12,000 tons in 1953; Lamb and Irving, 1955) than for any other purpose. Its use allows castings to be easily removed on cooling because the graphite gives the surfaces of molds a smooth finish. For this purpose amorphous graphite is mixed with clay, mica, or talc, and sand, and the mixture is pulverized.

An important, although not a large, use for graphite is in the manufacture of crucibles used in melting of nonferrous metals and alloys. The crucibles used must withstand temperatures as high as 2800° F and rapid changes from room temperature to such highs. For this purpose, crystalline flake graphite is necessary. According to the Bureau of Mines (Lamb and Irving, 1955), the United States imports between 3000 and 4000 tons annually. The nation appears to be becoming less dependent on this source, as carbon-bonded silicon carbide-graphite crucibles, which contain less and lower-grade than ordinary crucibles, are being manufactured.

A small, but critical, tonnage of amorphous lump graphite (about 1000 tons annually) is imported from Ceylon for the manufacture of carbon brushes for electric motors. Graphite for this purpose must be very free of impurities. Artificial graphite is unsatisfactory.

"Lead" pencils in the United States are made from finely ground very pure amorphous graphite from Ceylon and Mexico. No large tonnage is required, but this is an ancient and important use of graphite.

Consumption of natural graphite in the United States, by use, in order of decreasing amounts is in foundry facings, steel making, lubricants, crucibles, filler for dry batteries, and lead pencils. Among the many other uses of small amounts of graphite are in paints, polishes,

pump packings, bearings, brake linings, furnace bricks, rubber goods, adhesives, roofing granules, electrodes, powder metallurgy, and as a moderator in atomic piles.

The graphite in the California deposits generally occurs in flakes that are too small to command the best prices paid for the type of flake graphite that can be used in crucibles and refractories. California graphite is suitable for paints and foundry facings but the low grade and small size of the deposits makes competition with Mexican amorphous graphite unfavorable.

Artificial graphite, manufactured from amorphous carbon at extremely high temperatures in the electric furnace, is becoming more widely used. Data are not available on the relative amounts of artificial and natural graphite in use but the following quotation from Battelle Institute (1956) summarizes the more interesting and pertinent information on developments in artificial graphite.

Long used in electrothermic and electrolytic industries, graphite also has unusual high-temperature structural properties. Because of these properties, the material is being studied for possible use in nuclear-power and rocket applications, and the resulting data will enable design engineers to employ graphite in many cases where high-temperature stability is required. Because of their greater load-bearing capacity, artificial graphites are preferred for many graphite applications.

The physical properties of artificial graphite reflect its unusual structure according to L. D. Loch of Battelle. The material is composed of crystals that consist of two-dimensional layer planes stacked like playing cards in a deck and while bonding within the layers is very strong, bonding between the layers is weak. This makes graphite stable at high temperatures, and yet the easy slipage on planes also makes it a good lubricant. The material does not melt at atmospheric pressures, but sublimes at about 6500 F. Not being resistant to oxidation it must be protected by oxidation-resistant coatings.

The properties of graphite may vary widely even within the same grade. Bend strengths of different grades may vary from 1500 to 4500 psi. Tensile strength is about one-half the bend strength, while crushing strength is about double the bend strength. The material's strength increases with temperature, and at 3000 F it is one of the strongest of materials. With a thermal conductivity approaching metals and with low thermal expansion and elastic modulus graphite has excellent resistance to thermal shock.

The properties summarized above make artificial graphite highly useful in a number of fields. Thus in metallurgy it is used in dies and molds in many continuous-casting processes. Graphite is excellent for multiple extrusion of aluminum, and it is employed for crucibles and boats in the treatment of many metals, including semiconductor materials.

Graphite has helped to speed the development of rockets. Its properties have made it extremely valuable in combustion chambers and nozzles where it can withstand extreme temperature changes, and when coated, the erosive effects of gases moving at very high velocity. The material is also widely used in the construction of nuclear reactors.

The need for materials with adequate strength at high temperatures is one factor retarding the development of these fields. Artificial graphite can play an important part in breaking this bottleneck.

*Production and Markets.* The difficulty with which producers of domestic graphite compete with imported or artificial graphite is suggested by the small number of United States producers (three in 1953; Lamb and Irving, 1955), as well as by California's lack of production since 1935. The U. S. S. R. yields large quantities, but does not release statistics. The low quality of the graphite in most deposits in the United States, the small tonnage of any one grade of graphite consumed, and ample world supply are the principal causes of the smallness of the United States production.



Production of natural graphite in the United States has ranged from 4,000 to 10,000 tons annually in recent years, while imports have been between 26,000 and 54,000 tons annually.

Strategic minerals to be stockpiled in the United States now include crucible-grade crystalline flake graphite. The federal government purchased high-carbon amorphous lump graphite from Ceylon for the stockpile in 1955. In 1955, crucible-grade graphite was still eligible for a 50 percent Government loan under the Defense Minerals Exploration Administration program.

Prices paid for graphite vary greatly with the form and quality, as shown by the following summary of recent prices f.o.b. New York, quoted by the Oil, Paint and Drug Reporter for November 21, 1955, and by the U. S. Bureau of Mines (1955).

Imported amorphous, natural, up to 85% C, bgs., lb. -----	\$0.06-09½
Crystalline 88-90 percent C, powd., bgs., lb. -----	0.19-21½
Flake No. 1, 90-95 percent C, bgs. -----	0.29-31
Madagascar, c.i.f. New York, standard grades, 85-87% C, ton -----	235.
Amorphous, Mexican, f.o.b. point of shipment, metric ton -----	9-16

Purchasers of graphite in California are Pacific Graphite Company, 40th and Linden Streets, Emeryville, and 416 W. 8th Street, Los Angeles, and Los Angeles Chemical Company, 4545 Ardine Street, South Gate. Pacific Graphite Company imports a few hundred tons of graphite a year from Mexico, Ceylon, Bavaria, and Kenya; a very little artificial graphite is also used. The company does no refining but grinds and blends the various grades of graphite to make products used principally in paint pigments and foundry facings. Los Angeles Chemical Company imports a few carloads a year

of amorphous graphite from Mexico; no artificial graphite is used. Both companies are interested in purchasing carload lots only of 82 percent, or better, amorphous graphite and smaller amounts of amorphous lump and flake graphite now imported. No California deposits have been found which can meet either of these requirements.

As an example of transportation costs, graphite can be shipped by rail from Burnet, Texas, to Los Angeles for \$1.77 cwt., minimum 60,000 lbs.

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## GYP SUM

BY WILLIAM E. VER PLANCK

The 1953 production of gypsum in California was 1,199,489 short tons valued at \$2,855,983, which was about 10 percent of the United States production of gypsum. Rock gypsum is mined in the Little Maria Mountains, Riverside County; the Fish Creek Mountains, Imperial County; and near Cuyama Wash, Ventura County. Large tonnages of gypsite are mined in the southwestern part of the San Joaquin Valley. Not included in the production figures is the synthetic gypsum produced from salt works bittern as a by-product of magnesia manufacture. (See the section on magnesium and magnesium compounds in this volume.)

Although there are large undeveloped gypsum deposits in California, 200,000 to 300,000 tons a year of raw gypsum and finished gypsum products, aided by favorable transportation costs, are brought into the state. Raw gypsum comes by ship from San Marcos Island in the Gulf of California; raw gypsum and gypsum products come by rail from Nevada.

### MINERALOGY AND GEOLOGY

Gypsum is the natural calcium sulfate hydrate  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ . Most commercial gypsum is a massive material which contains a minimum of 90 percent of the mineral and is known as rock gypsum. Gypsite, formerly called gypsum earth, consists of gypsum mixed with sand or clay in earthy, fine-grained deposits and is also important commercially. Most commercial gypsite contains from 50 to 70 percent gypsum. Other less common varieties of gypsum are the platy, transparent type known as selenite, the fibrous type known as satin spar, and the massive white, sometimes translucent type known as alabaster. Gypsum is commonly associated with anhydrite ( $\text{CaSO}_4$ ), a mineral of little present commercial value.

Several additional calcium sulfate substances can be prepared in the laboratory by calcining gypsum under controlled conditions. These include two forms of the hemihydrate ( $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ ) and two forms of soluble anhydrite which may contain as much as one percent  $\text{H}_2\text{O}$ . These dehydration products can be easily rehydrated. All four may form in the commercial calcining kettle and therefore are of more than theoretical interest.

Most natural calcium sulfate minerals form through the evaporation of sea or saline lake waters, but some also occur in hydrothermal veins, in near-surface veins formed by deposition from ground water, and as replacements of limestone. In saline deposits, at least part of the calcium sulfate is believed to have originally precipitated as anhydrite and to have been altered to gypsum by the action of ground water.

Gypsite forms only in regions of little rain and fast evaporation. Calcium sulfate-bearing ground water is drawn upward by capillary action, and small gypsum crystals form at or close to the surface. On the west side of the San Joaquin Valley of California, most of the Tertiary formations contain gypsum along fractures or as part of the cement of sandstones.

In California the rock gypsum deposits that have been worked are in Tertiary non-marine sedimentary rocks

and in mildly metamorphosed pre-Cretaceous rocks. Most of the gypsite mined in California is obtained from Recent surficial deposits. A playa deposit of Quaternary age at Bristol Lake, San Bernardino County, was worked from 1906 to 1925; it was the largest single source of gypsum in California during that period.

*Quaternary Deposits.* Recent deposits of gypsite are mined at several localities along the southwest margin of the San Joaquin Valley from Little Panoche Creek to Maricopa; and additional tonnages are obtained from the playa at Saltdale, Kern County, and from Carrizo Plain, San Luis Obispo County. In the past gypsite has been mined also from the margins of old Kern Lake and along Cottonwood Creek, Kern County; near Palmdale, Los Angeles County; and near Corona, Riverside County.

Three types of gypsite deposits have been recognized in California; those that form caps on upturned gypsiferous beds, those that occur along the margins of periodic lakes, and those that have formed in the beds of dry washes. The gypsite that has formed on the outcrops of gypsiferous rocks is called "cap gypsum." Probably most of the deposits are of this type. Gypsite is derived from the Maricopa shale (upper Miocene) and Tulare formation (Pleistocene) at McKittrick, the Paso Robles formation (Plio-Pleistocene) at Kettleman Hills, the Tejon formation (Eocene) near Coalinga, the Vaqueros formation (lower Miocene) at Tumey Gulch, the Kreyenhagen formation (Eocene and Oligocene) near Ortigalita Creek, and the Domengine formation (Eocene) in the Panoche Hills.

Cap gypsum deposits closely follow the present surface, although the overburden is thin or lacking on the upper parts of hillsides and thicker toward their bases. The bottom contact of some deposits is sharp, but the gypsite ordinarily grades into the underlying material. Examples include some of the deposits at McKittrick, the idle Carissa mine in Carrizo Plain, the Griffin deposit at Tumey Gulch, and the Valley View deposit in the Panoche Hills.

The gypsite deposits along the margins of periodic lakes are efflorescent deposits derived from ground water in the soil. The lake water itself may never have been saturated with gypsum. Gypsite bodies thus formed are irregular lenses that lie with a sharp contact on the lake beds. Solution cavities are a characteristic feature. The deposit on the south margin of old Kern Lake, the Daly deposit near Saltdale, and probably H. M. Holloway Inc.'s Avenal Gap mine belong to this class.

The gypsite that has formed in the beds of dry washes is called "channel gypsum" by the miners. Southwest of McKittrick two such deposits have been worked. They are long, narrow deposits that closely follow the present dry washes and seem to have formed in the stream beds by the evaporation of gypsiferous ground water. The gypsite lies beneath as much as 5 feet of slightly consolidated sand and gravel containing shale fragments. Toward the base the gypsite grades into gypsiferous sand and clay, and in places it rests on creek gravel containing selenite fragments as much as an inch long.





FIGURE 1. Schist and gypsum, Little Maria Mountains, Riverside County. Coarsely crystalline gypsum of high purity is associated with bluish-gray quartz biotite schist.

The Lost Hills deposits, operated by H. M. Holloway, Inc., are the largest known gypsite deposits in California, and have features of both the channel and lake-margin types. Gypsite bodies are scattered along the southwest side of the Lost Hills for a distance of 5 miles and are largest where existing washes cut through the hills. Much of the gypsite occurs as flat-lying lenses, some as much as 20 feet thick, in silty sand and clay. Typically the gypsite is within 3 feet of the surface, but the overburden is as much as 10 feet thick. Some gypsite bodies are elongate and occur in or along the existing washes.

Information gained during mining a very considerable tonnage of gypsite as well as from a program of drilling and sampling reveals that the gypsite deposits are composite bodies composed of several gypsite lenses. Sand and gravel lenses are encountered as well as pebbles scattered through the gypsite. The gypsite operator believes that most of the gypsite was laid down by water as a sedimentary deposit. At some period less arid than the present, occasional floods of storm water may have come from the Temblor Range and have been temporarily ponded on the southwest side of the Lost Hills, which

acted as a barrier. This flood water may have washed gypsite from the Temblor foothills where remnants of gypsite deposits still exist. Probably most of the floods reached no farther than the Lost Hills where they deposited their loads of gypsite in relatively quiet water, more or less separated from non-gypsiferous material by hydraulic classification. Sometimes water appears to have broken through the Lost Hills, scouring channels through deposits previously formed and distributing gypsite along the washes. Probably the amount of rainfall was critical. With less than the critical amount, gypsite would not have been carried as far as the Lost Hills; and with more, the Lost Hills barrier would not have halted the flood waters.

Gypsum in the form of selenite crystals dispersed in mud occurs in Bristol Lake, San Bernardino County, and in the neighboring Cadiz and Danby Lakes. Gypsum from Bristol Lake supplied a large plaster mill at Amboy from 1906 to 1925; there has been no production from Cadiz Lake or Danby Lake.

Bristol Lake is filled with brine-saturated fine sediments covered by a thin salty crust. In the central part, a bed of salt (sodium chloride) permeated with a meager amount of sodium-calcium chloride brine, lies within 4 to 8 feet of the surface. Deeper salt beds are known to exist. Selenite crystals and celestite nodules are found in the mud near the lake margins and outside of the central salt-bearing area.

Gypsum has been found at or close to the surface and within a mile of the shore all around the lake, but it is most abundant on the west and north sides. The gypsum ranges in character from clean, white, granular material to salty silt containing selenite crystals. Some crystals are as much as an inch in maximum dimension. In the areas being worked in 1909, gypsum extended from within a foot of the surface to an unknown distance below the level of the brine which was encountered within 8 feet of the surface.

Danby Lake, like Bristol Lake, contains salt beds, but the brine is of the chloride-sulfate type. Lenticular concentrations of selenite crystals occur in the mud of the central salt-bearing parts of the lake, as well as along the margins, and to depths of at least 50 feet. Gypsum does not occur in the massive salt deposits. The muds do

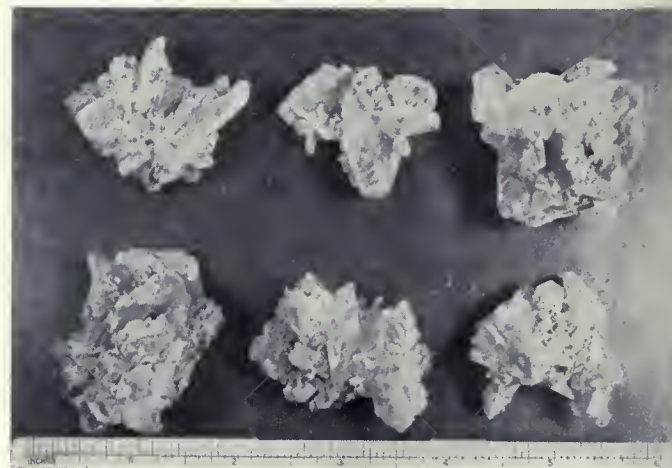


FIGURE 2. Selenite crystals from Danby Lake. Reprinted from *Division of Mines Bulletin 163*.



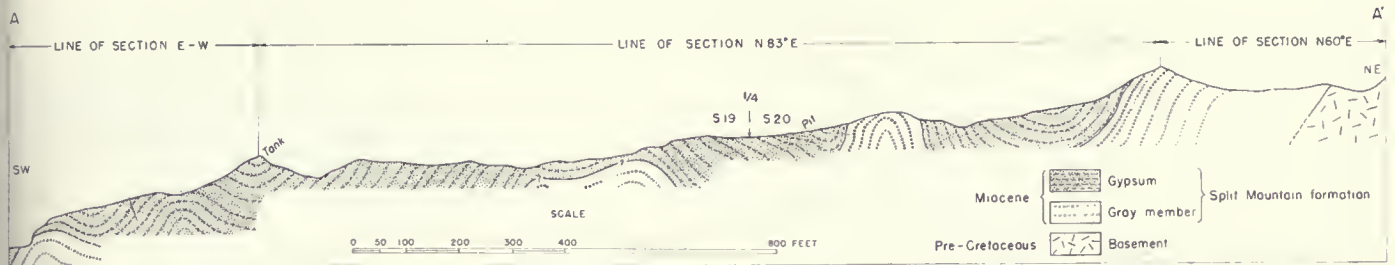


FIGURE 3. Geologic section through Fish Creek Mountains gypsum deposit, Imperial County. Reprinted from *Division of Mines Bulletin 163*.

contain, however, crystals of selenite intimately mixed with salt crystals or, more rarely, mirabilite.

The extent and character of the gypsum deposits in Cadiz Lake are not generally known.

**Tertiary Deposits.** Rock gypsum deposits of Tertiary age include the one worked by the United States Gypsum Company in the Fish Creek Mountains, Imperial County. This operation is the largest gypsum mine in the state. The deposit, which is at the north end of the Fish Creek Mountains, is part of a deposit that was formerly much more extensive, but it has been dissected by erosion. In the mine area the gypsum beds have been preserved in a shallow synclinal basin 3 miles long and half a mile wide. The beds, except for severe local contortions in the gypsum, dip uniformly at angles of from  $25^{\circ}$  to  $35^{\circ}$  toward the synclinal axis.

The gypsum is part of a section of Miocene sedimentary rocks that lies on a pre-Cretaceous basement of metamorphic rocks intruded by coarse gneissic granite. The gypsum is underlain by the Split Mountain formation which in its lower part consists of coarse, arkosic, red-weathering sandstone with conglomerate beds composed of cobbles of the older rocks. The upper part is a gray boulder conglomerate with subordinate layers of gray, arkosic sand. In most places this sand immediately underlies the gypsum. Overlying the gypsum is the Imperial formation, which consists of limonite-cemented quartz sand and clay. These beds have been largely removed by erosion. Eastward the underlying Split Mountain formation pinches out and is overlapped by the gypsum. Other large but less accessible remnants of the original deposit are known to exist to the south, and there are extensions westward into San Diego County.

Another Tertiary deposit is worked by the Monolith Portland Cement Company in Quatal Canyon near Cuyama Wash, Ventura County. This deposit consists of a single bed of massive brown gypsum 10 to 30 feet thick that can be traced for at least 7 miles. The gypsum is contained in the Quatal red clay, a non-marine facies of the upper Miocene Santa Margarita formation. The Blue Diamond Corporation owns patented claims adjoining the Monolith Portland Cement Company's property on the northwest.

A second gypsiferous zone in the Cuyama Wash region occurs in the middle Miocene Caliente red beds southwest of the Quatal Canyon deposit. It consists of thin beds of gypsum and gypsiferous beds from which gypsite deposits have been derived. Masses of alabaster as much as 10 feet in maximum dimension occur in it. Exploratory work has been done in numerous places, but only a small tonnage of gypsum has been shipped. The terrestrial clays that contain both groups of gypsum

deposits grade into marine sediments northwestward along the strike; to the southeast the clays grade into coarse elastic sediments (Dibblee, T. W., Jr., personal communication).

In the northern foothills of the Avawatz Mountains, San Bernardino County, gypsum, salt, and celestite occur in Pliocene (?) lake beds in the Death Valley fault zone near its junction with the Garlock fault zone. The lake beds occur in two roughly parallel zones discontinuously exposed for a distance of about 9 miles. They consist of a gypsum-bearing unit, a salt-bearing unit, and saline-free sedimentary rocks that enclose the gypsum and salt beds. The gypsum-bearing unit consists of 600 to 800 feet of predominantly light tan colored sedimentary rocks in which gypsum occurs as relatively thin beds alternating with greenish, gypsiferous clay. Gypsum beds are most abundant near the base of the gypsum-bearing unit as interpreted by Durrell (1953, p. 17) and form from a small fraction to as much as two-thirds of the lower 50 feet. Celestite occurs in the gypsum-bearing unit, particularly in the western part of the deposit. Although the gypsum has been well explored, there has been no production.

Gypsum has been mined at China Ranch, San Bernardino County, from the upper Pliocene (?) China Ranch beds. The gypsum was obtained from a 20-foot gypsiferous zone composed of gypsum beds from 6 inches to 3 feet thick separated by as much as 3 inches of shale. The gypsum is white and of medium grain size. The beds dip as much as  $25^{\circ}$ .

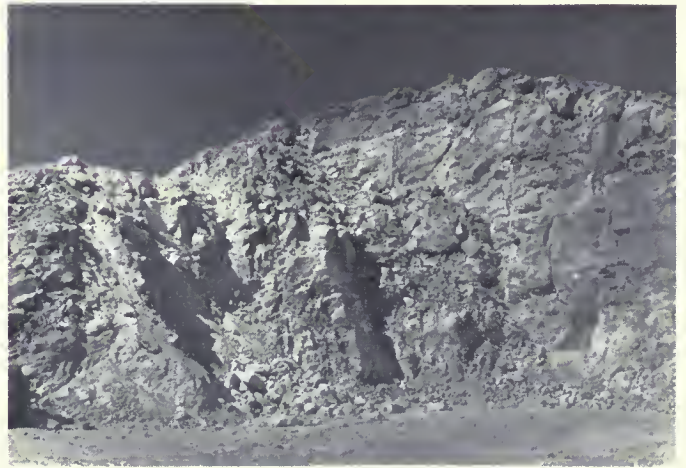


FIGURE 4. Photo showing a portion of the United States Gypsum Company quarry, Fish Creek Mountains. The quarry face is more than 100 feet high. Gypsum is hauled to Plaster City, where it is made into plaster, wallboard, and other calcined gypsum products.



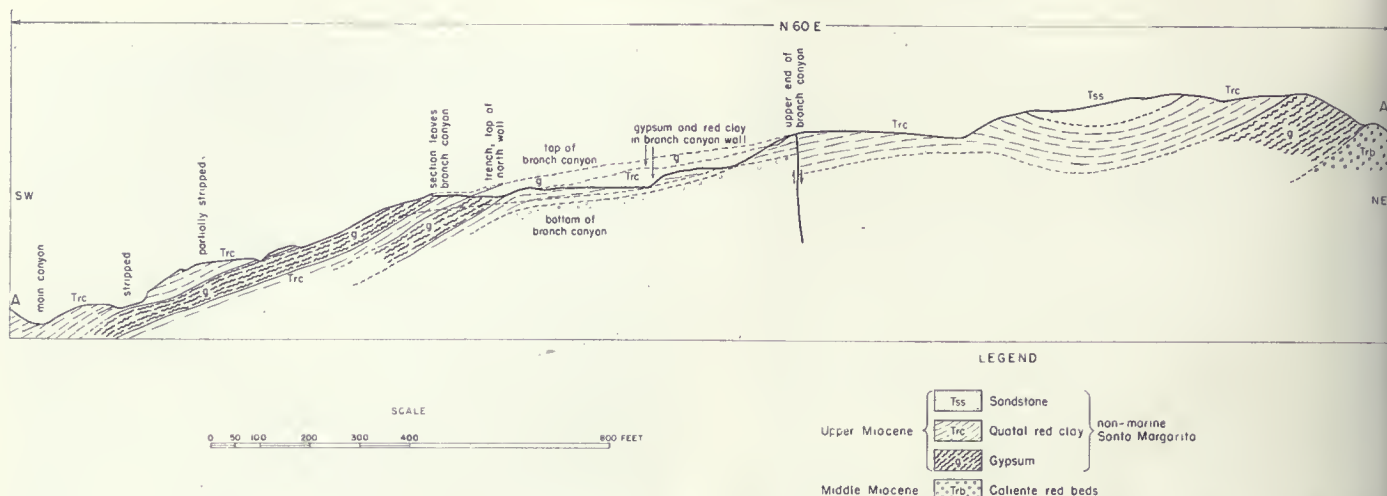


FIGURE 5. Geologic section through Quatal Canyon gypsum deposit, Ventura County. Reprinted from *Division of Mines Bulletin 163*.

Similar but smaller Tertiary deposits are found at Owl Hole, Copper Canyon and Furnace Creek in the Death Valley area. Other Tertiary deposits, some of which have been worked, are near Point Sal, Santa Barbara County; in Mint Canyon, Los Angeles County; and on the Mule Shoe Ranch, San Benito County.

**Pre-Tertiary Deposits.** Pre-Tertiary deposits of gypsum occur in the Little Maria Mountains, Riverside County, where the Midland operations of the United States Gypsum Company and the Garbutt and Oreutt deposit are located. The gypsum beds form part of a series of slightly metamorphosed sedimentary rocks that trends across the range from east to west, a distance of 3 to 4 miles. The sediments are in fault contact with intrusive granitic rocks on the north and are bordered on the south by gneiss. The rocks of the gypsum belts are quartzite, crystalline limestone, and quartz-albite-mica schist that dip  $50^{\circ}$ - $80^{\circ}$  NW. Gypsum occurs in the limestone as persistent beds as much as 50 feet thick and in the schist as lenticular bodies that have a more limited extent. In places beds from 60 to 150 feet thick have been worked for strike distances of up to 700 feet. The gypsum is a coarse-grained snow-white aggregate of transparent grains. In many places it contains thin layers and lenses of schist, and schist is present also in gypsum interbedded with limestone. Anhydrite is present at depth and is the mineral from which the gypsum has formed. In the United States Gypsum Company's underground workings there is evidence that the extent of the alteration of anhydrite to gypsum depends on the presence of fractures and other openings that allowed the access of water. Similar but undeveloped deposits have been found in the Maria Mountains, the Palen Mountains (Hoppin, 1954), and the Riverside Mountains, Riverside County.

A pre-Tertiary deposit in unmetamorphosed rocks occurs at the south end of Mesquite Valley 12 to 13 miles from U. S. Highway 91 and the Union Pacific Railroad near the California boundary. This area contains an extension of the Triassic and Permian sedimentary rocks that crop out extensively in southern Nevada. Two or more gypsiferous zones as much as 50 feet thick can be traced for 1 to 2 miles. The gypsum is associated with

black, thin-bedded, cherty limestone, sandy limestone, and brown shale that appear to be members of the Permian Kaibab formation.

#### MINING

Gypsite commonly is mined with carryall scrapers. Deposits are prospected with bulldozer trenches or earth augers, and little development is necessary other than the construction of truck-loading chutes. Much of the gypsite is loaded directly from the scrapers into the trucks that carry it to the consumers.

Rock gypsum must be drilled and blasted. A majority of the gypsum mines in California have been open-cut operations, and the maximum ratio of overburden to gypsum is about  $1\frac{1}{2}$  to 1. The Fish Creek Mountains deposit has been developed by means of an open cut which in 1942 was 3,000 feet long and 100 feet high. Most smaller mines use wagon drills or jackhammers, and benches 10 to 15 feet high are maintained. Flat-lying deposits covered by much overburden and steeply dipping deposits have been worked by open stope or room-and-pillar methods in California, but in 1955 no underground gypsum mines were in operation.

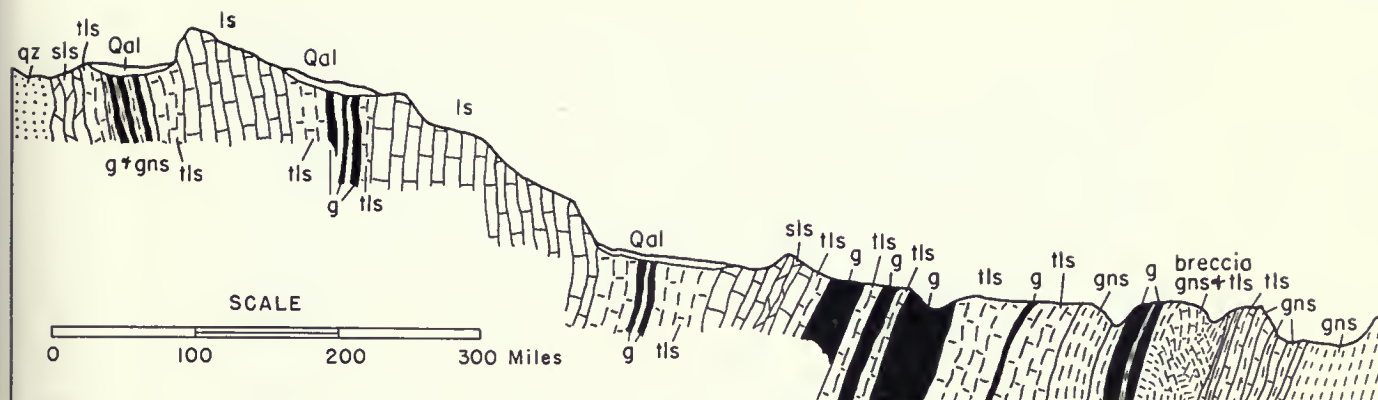
#### USES AND TREATMENT

The principal commercial uses of gypsum depend on three facts: (1) when gypsum is partly dehydrated by calcination at a moderate temperature, a material forms that sets or hardens when it is mixed with water; (2) gypsum improves the texture of certain types of soil; and (3) it retards the naturally fast setting time of portland cement.

The principal consumers of crude gypsum, the plaster industry, agriculture, and the portland cement industry, probably use 1 to  $1\frac{1}{2}$  million tons of gypsum a year in California. The consumption of agricultural gypsum in California is in the range of 600,000 to 700,000 tons a year. A roughly equal amount is required by the plaster industry, and the portland cement industry consumes 100,000 to 150,000 tons a year.

In agriculture the most important function of gypsum is the conditioning of alkali soils. By raising the ratio of calcium ions to sodium and potassium ions, the clay





EXPLANATION: Qal - Alluvium; ls - Crystalline limestone; sls - Siliceous limestone; tls - Tremolitic limestone  
qz - Quartzite; g - Gypsum; gns - Green schistose rocks

FIGURE 6. Geologic section through Little Maria Mountains gypsum deposit, Riverside County.  
*Reprinted from Division of Mines Bulletin 163.*

particles are prevented from deflocculating and becoming very hard when dry. Gypsum also changes the harmful black alkali (sodium carbonate) to the less harmful white alkali (sodium sulfate). Gypsum is a source of both sulfur and calcium and is particularly useful on soils that are not acid.

For agricultural use, rock gypsum, gypsite, and anhydrite appear to be of equal value when compared on an equivalent basis (Rollins, 1951, p. 107). For example 100 pounds of pure rock gypsum is the equivalent of 143 pounds of gypsite containing 70 percent gypsum, or of 79 pounds of pure anhydrite. In California 90 percent of the agricultural gypsum consumed is gypsite produced within 150 miles of the farms, and rock gypsum comprises most of the remainder. For agricultural use, rock gypsum is finely ground, commonly to 85 percent minus 100 mesh; but gypsite requires no preparation.

In the plaster industry, gypsum is calcined under carefully controlled conditions; and the resulting material, called stucco, is further processed into wallboard, lath, or plasters for a host of purposes. Rock gypsum containing at least 92 percent  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  is the raw material used, although in the past, plaster has been made from gypsite. In the preparation of gypsum for calcining, quarry-run rock is reduced with jaw crushers or gyratories. Hammer mills are widely used as secondary crushers and primary grinders; and the final grinding is often done with Raymond roller mills.

Calcining must be done under temperatures that range from 300°F. to 400°F. Overcalcining produces dead-burned gypsum (anhydrite) which will not rehydrate. Uncalcined lumps of gypsum act as a powerful accelerator of the set and are highly objectionable because their presence causes a non-uniform product.

Batch machines called kettles are used for most grades of stucco. The typical kettle employed in California plants is a brick-lined steel cylinder heated from below by an oil- or gas-fired furnace and also by four large horizontal flues through which the furnace gases pass. The boiling action caused by the water of hydration being driven off produces the necessary agitation, but

additional action by rabble arms close to the bottom prevents sticking. A charge consists of 10 to 20 tons of gypsum ground to 80 percent minus 100 mesh. During calcination, which takes about 2½ hours, the temperature gradually rises from about 250°F. to 340°F. The finished batch is dumped into a hot pit before removal to storage bins.

Stucco can be made by continuous methods, but at present it is not possible to make a product sufficiently uniform for all purposes. Two plants in California use the Raymond Imp mill, which is essentially a hammer mill through which are passed the hot gases from an adjacent furnace. Gases at 1400°F. together with raw gypsum crushed to 1 inch or finer enter the mill, and stucco is withdrawn at 360°F. to 410°F., 90 percent minus 100 mesh. It is then separated from furnace gases and steam and put in storage bins.

Hardwall plaster is made from kettle stucco reground dry in tube mills. The ground stucco is then mixed with fiber, sometimes sand or perlite, and a retarder. For casting plaster, kettle stucco is reground in Buhr mills.

In California, gypsum wallboard and lath are made both from kettle stucco and from stucco produced by continuous methods. These products are made on Ehram machines, which are almost entirely automatic. Modern plaster plants have capacities of as much as 225,000 square feet of board products a day.

In 1955, five calcining plants were operating in California, one in the San Francisco Bay area, two near Los Angeles, and two in the southeastern desert area. The Kaiser Gypsum Company owns two plants, one at Long Beach, the other at the Port of Redwood City, that consume gypsum brought in special ships from San Marcos Island, Baja California. The Redwood City plant was destroyed by fire in June 1955. The United States Gypsum Company also owns two plants. One, at Plaster City, Imperial County, uses gypsum brought from the Fish Creek Mountains deposit 25 miles to the north over a private railroad; the other, at Midland, Riverside County, processes gypsum mined in the nearby Little Maria Mountains. The fifth plant, at South Gate, is owned by Pabco, Inc., and it is supplied by rail from the





FIGURE 7. Photo showing gypsum workings, Garbutt and Orcutt deposit, Little Maria Mountains. From 1946 to 1950 gypsum was quarried from this deposit and ground for agricultural use. The gypsum is associated with quartz biotite schist.

company's deposit near Henderson, Nevada. In addition, plaster products are shipped into California from plants at Gerlach and Arden, Nevada.

The portland cement industry uses raw gypsum as a retarder. About 10 pounds of gypsum consisting of at least 92 percent  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  are added per barrel of cement. Probably most of the mills in California are accustomed to using, and therefore specify, gypsum that is crushed to plus  $\frac{3}{8}$ -inch and minus  $1\frac{1}{2}$ -inch. Some, however, specify finely ground gypsum; and a few are equipped to handle both pebble and finely ground gypsum.

#### PRICES

Although in 1952 the average value of crude gypsum at the mine was reported by United States producers to be \$2.72 a ton (North, O. S., and Jensen, N. C., 1954), most figures for rock gypsum are nominal. The only California production costs available are those of the defunct Inca operation which produced agricultural gypsum in the Little Maria Mountains from 1946 to 1950 (Ver Planck, 1952, p. 100). The mining and grinding of bulk gypsum (ground to 100 percent minus 10 mesh) cost about \$3.00 a ton, and of sacked gypsum (100 percent minus 50 mesh), \$6.00 a ton.

In California, gypsite for agricultural use sells for between \$1.00 and \$2.00 a ton at the mine, depending on the grade. Some agricultural gypsum is sold at the mine, but the price usually includes delivery and sometimes spreading it on the fields. In the San Joaquin Valley gypsite containing 50 to 70 percent gypsum sells for between \$6.00 and \$7.00 per ton delivered and spread. Ground rock gypsum for agricultural use sells for \$14.00 a ton delivered or as much as \$18.00 a ton if spreading is included.

#### MARKETING

Gypsum is a low-priced, widely distributed commodity that is of value only when it can be economically mined and transported to consuming centers. The mining of rock gypsum requires a substantial investment in equipment; and deposits are of little economic value unless they contain many thousand tons of uniform, high-grade material. Because little equipment is necessary, much smaller deposits of gypsite can be profitably worked if a local market exists.

Freight charges represent a substantial portion of the price of crude gypsum to the consumer. The maximum distance that rock gypsum is hauled by rail in California is a little less than 300 miles; gypsite is seldom hauled more than 150 miles.

Plaster manufacturers seldom purchase crude gypsum. The plaster industry is characterized by integrated companies that operate large calcining and manufacturing plants supplied with crude gypsum from low-cost, captive operations. These companies own or control large deposits of gypsum, and many of them are engaged in a search for additional reserves. Most of the undeveloped gypsum deposits in California are too small and irregular to support a modern calcining plant.

The production of gypsum products such as hardwall plaster and wallboard requires a large investment of capital. Expenditures of  $1\frac{1}{2}$  to 2 million dollars have been reported for the building or reconstruction of calcining and wallboard plants. Moreover, competition is keen, and marketing channels must be established.

In addition to calcined products, the plaster industry furnishes the uncalcined rock gypsum that is used in relatively small amounts by the portland cement industry and in agriculture. These products are produced by the large capacity crushing and grinding plants that are primarily engaged in preparing gypsum for calcina-



tion at costs that can seldom be equaled by plants that prepare uncalcined gypsum only.

Most of the agricultural gypsum consumed in California is used in the San Joaquin Valley and 90 percent of the supply is gypsite produced within 150 miles of the farms. Elsewhere in California, ground rock gypsum brought from plants in Nevada or southern California is used almost exclusively. Because a high proportion of the cost of gypsum to the farmer is represented by handling charges, local markets can be developed for gypsite with a gypsum content of 70, 60, or even 30 percent. In addition, gypsite deposits can be developed and mined with relatively little equipment. Ten producers of agricultural gypsum, some of which operate more than one deposit, were registered with the State Bureau of Chemistry for the fiscal year ending June 30, 1956.

The producer of agricultural gypsum, including both gypsite and high-grade, ground, rock gypsum, must comply with the regulations of the State Department of Agriculture. The Agricultural Code requires that a producer must be registered with the State Bureau of Chemistry and that each lot or package of gypsum must be properly labeled. Although the law does not specify the minimum content of agricultural gypsum, frequent inspections are made to see that the product conforms

with the producer's own guarantee. The mortality rate among producers of agricultural gypsum has been high, and probably the greatest single cause is failure to produce gypsum of the guaranteed quality.

Most portland cement plants purchase crude gypsum. Only one company in California, the Monolith Portland Cement Company, quarries gypsum for its own use. Two other companies own gypsum deposits that are held in reserve in case of an emergency. Portland cement plants desire a uniform, dependable supply of gypsum; and many require a long-term guarantee. In addition, the gypsum producer who supplies the portland cement industry must find a market for off grades and sizes that are not acceptable to the portland cement plant.

#### HISTORY OF PRODUCTION

The outstanding feature of California's gypsum industry is the rapid increase in production in recent years. This growth in part reflects the increase in building activity. The application of gypsum to soils bearing certain crops has been greatly stimulated by the policy of the Federal Production and Marketing Administration, which makes payments to farmers for the application of agricultural gypsum on the basis of its contained sulfur content.

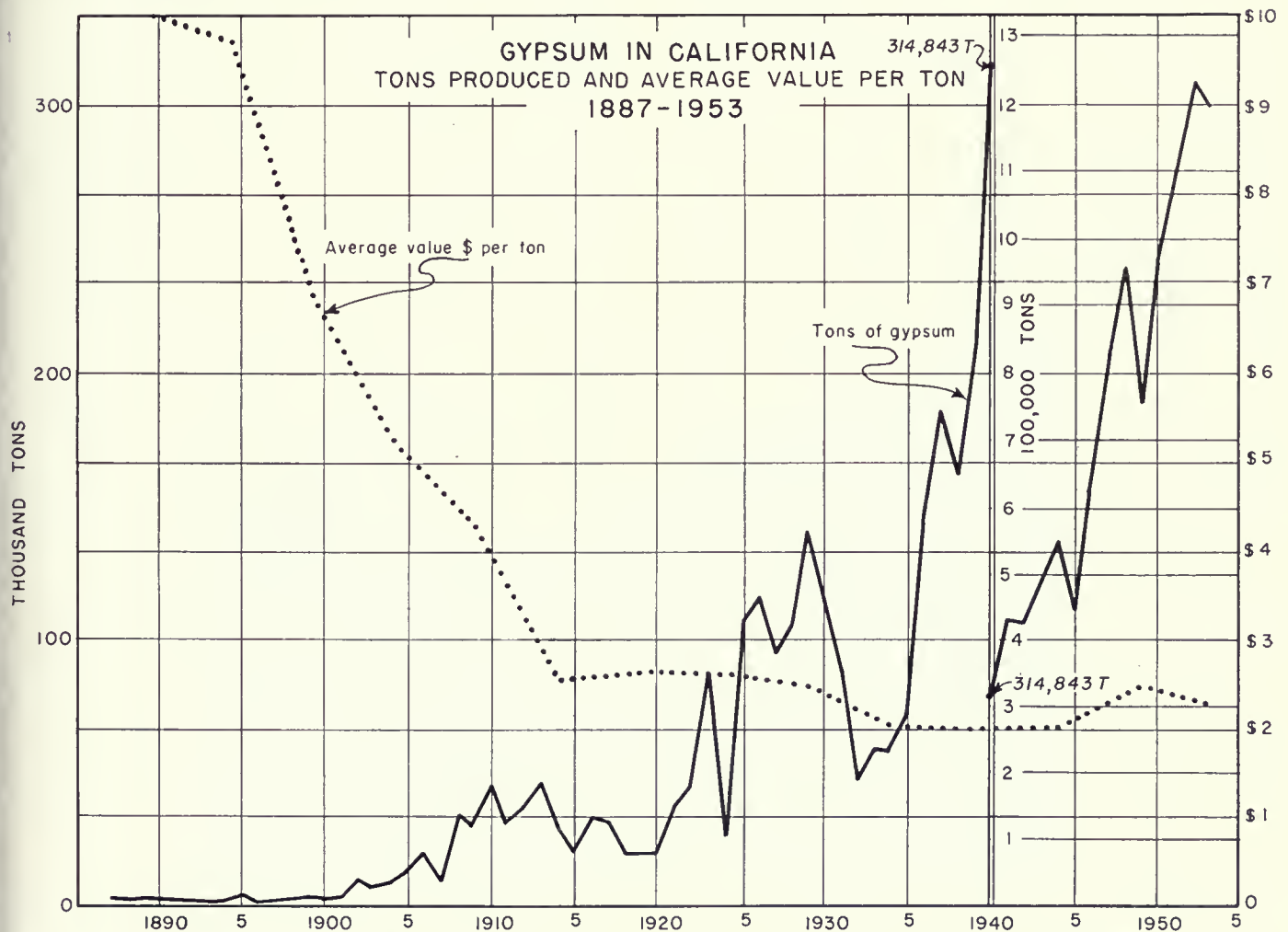


FIGURE 8. Chart showing amount and average value per ton of gypsum produced in California, 1887-1953.





FIGURE 9. Photo showing gypsite operations of H. M. Holloway, Inc., at Lost Hills, Kern County. Carry-all scrapers load the gypsite into trucks that carry it to farms in the San Joaquin Valley.

Although it has been stated that the earliest use for gypsum in California was for agriculture, the Golden Gate plaster mill of Lucas and Company at San Francisco was in operation before 1875. It received at least part of its requirements from the Point Sal mine, Santa Barbara County. In 1884 a mill at Los Angeles was grinding gypsum for agricultural use. Before 1880, Lucas and others were importing crude gypsum from Lower California, probably San Marcos Island (Hanks, 1884, p. 228).

The Point Sal mine was closed in 1889, but within the next 10 years other producers took its place. Among them were the Alpine Plaster Company and the Fire Pulp Plaster Company at Palmdale, Los Angeles County; the Paoli mine and the Coalinga mine, Fresno County; and Captain Fauntleroy's deposit on Cottonwood Creek, Kern County. All of these operations were closed by 1910. The Pacific Cement Plaster Company began operations at Amboy, San Bernardino County, in 1906 and in succeeding years built the largest calcining plant in California of that time. This company was bought out by the United States Gypsum Company in 1919. In 1916 and 1917 the Acme Cement Plaster Company operated a gypsum mine at China Ranch, San Bernardino County. Gypsum, which was produced from underground workings at the rate of 1,000 tons a month, was shipped by rail to Los Angeles where it was calcined.

Perhaps as early as 1910 the United States Gypsum Company began searching for a deposit in California. The deposits in the Little Maria Mountains were selected, and a 4-year development program was begun in 1916. As stated above, however, this company purchased the plant and deposit at Amboy in 1919; and it produced gypsum products there for about 5 years. When the Santa Fe Railway's Ripley branch was built through Midland in 1922, production of gypsum in the Little Maria Mountains became feasible, and operations were transferred there. The company completed a crushing and grinding plant at Midland in 1925, the output of which was largely portland cement retarder; and in 1928 a calcining plant of 300 tons daily capacity was added. A wallboard machine was installed in 1934, and



FIGURE 10. Photo showing gypsite operations of Superior Gypsum Company in Carrizo Plain, San Luis Obispo County. A view of the gypsite pit. The loading slot is sunk in the pit floor and does not reach the base of the deposit.

by 1944 the capacity of the Midland plant had been increased to 800 tons of calcined products a day.

The Fish Creek Mountains deposits were known at an early date, but they were not developed on a significant scale until the San Diego and Arizona Railroad was built in 1920. At about that time the Imperial Gypsum Corporation acquired a large portion of the Fish Creek Mountains deposit and built a narrow gauge railroad from it to the point on the standard gauge line that is now called Plaster City. In October 1922 crude gypsum began to be shipped to Los Angeles where it was sold to a calcining plant. Two years later the operation was sold to the Pacific Portland Cement Company which, in addition to its cement plants, owned gypsum operations in northwestern Nevada. The new owner built a calcining plant of 300 tons daily capacity at Plaster City. During World War II the Pacific Portland Cement Company began to withdraw from the gypsum business, and the Fish Creek Mountains deposit was sold to the United States Gypsum Company in July 1945. This company immediately undertook a program of modernization and expansion. Since its completion, a major proportion of California's gypsum production has passed through Plaster City, although the United States Gypsum Company still operates the Midland plant.

The wallboard operation of Pabco Products Incorporated at South Gate originated before 1918 as the Schumacher Wall Board Corporation. This company was one of many in California that produced gypsum products from purchased stucco up to the 1930s. Most of these companies were absorbed or went out of business as the primary gypsum producers began to operate their own wallboard plants. The Schumacher Wall Board Corporation, however, installed calcining equipment and acquired gypsum deposits in southern Nevada; and about 1939 it began producing stucco for its own use. The company became a division of Pabco Products Incorporated shortly after World War II.

The Blue Diamond Corporation can be traced back to the Blue Diamond Materials Company which began producing plaster from purchased gypsum in Los Angeles



in the early 1920s. About 1925 it acquired its own deposits near Arden, southern Nevada, and began shipping gypsum from them to the calcining plant in Los Angeles. In 1941 the company transferred its manufacturing operations to Nevada.

The calcining plant in Long Beach has had several operators. It was built in 1924 and 1925 by the Standard Gypsum Company which was organized in 1922 and had a gypsum operation in northwestern Nevada. Production at Long Beach began in 1925, using crude gypsum mined at San Marcos Island, Baja California, by a subsidiary. In 1932 or 1933 the Standard Gypsum Company ceased operating and leased the Long Beach plant to the Pacific Portland Cement Company. This company operated it until 1941, but it was idle during World War II. After the war Henry J. Kaiser formed the Standard Gypsum Company of California, which leased the Long Beach plant from the old Standard Gypsum Company. The plant was rebuilt, a wallboard machine added, and production was resumed in 1947. A year later Kaiser Gypsum Company was formed to take over the Standard Gypsum Company holdings.

The wallboard plant at the Port of Redwood City was built by the Pacific Portland Cement Company in 1941. Although calcining equipment was installed, the board plant initially used stucco produced by the company in northwestern Nevada. About 1947 the Redwood City plant began calcining crude gypsum purchased from other companies. In 1949 Kaiser Gypsum Company purchased the plant and operated it until it was destroyed by fire in the summer of 1955.

The Monolith Portland Cement Company began producing gypsite for its own use from a deposit near McKittrick in 1940. A search was made for a substitute for this comparatively small deposit, and the one in Quatal Canyon was selected. Quarrying began in 1941. During the first year, the deposit was worked for the

Monolith Portland Cement Company by A. H. Lange, a contractor; but since that time the cement company has been the operator.

Although agricultural use was one of the earliest markets for gypsum in California, the annual consumption by agriculture did not exceed 25,000 tons until 1939. In 1944, nearly 400,000 tons were used; and agriculture consumed a record 708,593 tons in 1952. A portion of the agricultural gypsum used in the San Joaquin Valley has come from the Koehn Lake deposit, eastern Kern County. This deposit was discovered in 1909 and supplied a small plaster plant in 1910-13. Since 1926 almost all of the output has been used in agriculture. Gypsite was first produced in the Lost Hills area, Kern County, in 1930. The H. M. Holloway Company, which has become one of the largest gypsum producers in California, first reported production from the Lost Hills in 1934. For the fiscal year ending June 30, 1956, ten producers of agricultural gypsum were registered with the State Bureau of Chemistry.

At least two deposits of rock gypsum have been worked for agricultural gypsum alone. One is the Mule Shoe Ranch deposit, San Benito County, which was operated by the Triangle Fertilizer Company in 1938-42 and the Monterey Gypsum Company in 1945 and 1946. The other is the Garbutt and Oreutt deposit in the Little Maria Mountains, Riverside County. This deposit, consisting of five claims patented prior to 1919, was acquired by F. A. Garbutt and W. W. Oreutt in 1920. Exploration, including diamond drilling, was carried out in 1945; and in 1946 the deposit was leased to a Fresno company, the American Gypsum Company. The latter employed the Utah Construction Company to work the deposit and prepare agricultural gypsum in a grinding plant at Inca Siding near Midland. In 1948 the Utah Construction Company acquired an interest in the operation. Work began in September 1946 and continued



FIGURE 11. Photo showing gypsum quarry of Monolith Portland Cement Company, Quatal Canyon. The gypsum beds exposed in the face beyond the shovel are enclosed in the Quatal red clay member of the upper Miocene Santa Margarita formation.



intermittently until June 30, 1950, when the operation was abandoned, and the lease was terminated. During this period about 60,000 tons of agricultural gypsum were mined and shipped.

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## IODINE

BY WILLIAM E. VER PLANCK

All of the crude iodine recovered in the United States is produced in California. Two companies in the Los Angeles area furnish a substantial proportion of the United States' requirements. The remainder is imported from Chile and Japan.

**Occurrence.** Iodine, although a widely distributed element, occurs in small amounts and has not been found uncombined with other elements. Iodine-bearing minerals occur with certain silver and lead ores. The double salt dietzite  $[\text{Ca}(\text{IO}_3)_2 \cdot \text{CaCrO}_4]$ , the calcium iodate lautarite  $[\text{Ca}(\text{IO}_3)_2]$  and perhaps other iodates are found in Chilean caliche. Iodine has been detected in plants and animals, particularly marine plants and animals, and apparently is essential for organisms. Certain kinds of seaweed are a commercial source. Iodine occurs in artesian water in Java and Italy and in brine associated with natural gas in Japan. Salt water produced with oil from certain oil wells contains iodine in recoverable amounts. Most of the world's supply, however, has come from caliche deposits in Chile.

**Localities.** In California, recoverable amounts of iodine are present in the brines produced with oil in the Dominguez, Playa del Rey, Inglewood, Seal Beach, and Long Beach oil fields in the Los Angeles area. Scattered wells in other California oil fields yield iodine-bearing brine, but the cost of collecting it is prohibitive. These brines contain only  $2\frac{1}{2}$  to 3 percent dissolved solids, almost entirely sodium chloride. Iodine is present in amounts of as much as 140 parts per million, and is thought to be in the form of sodium iodide. The following analysis is representative of the iodine-bearing brines, although plant feeds are usually somewhat richer in iodine (Sawyer, 1949, p. 1550, Table III, Brine D).

	Parts per million
Iodine .....	50
Sodium .....	9,407
Calcium .....	351
Magnesium .....	211
Chloride .....	15,200
Bicarbonate .....	799
Sulfate .....	5
Silica .....	42
Iron oxide and alumina .....	7

Iodine is recovered from the water that accompanies the oil pumped from the oil wells. This water with its residual oil content is an objectionable waste that could not be discarded in a metropolitan area without some cleaning treatment. Cleaning of the water is also an important preliminary step in the recovery of iodine and thus accomplishes two purposes. Under present conditions the cost of collecting the oil field waste water cannot be borne by the iodine alone, and the only usable supplies of raw material come from fields yielding abundant iodine-bearing brine that must be gathered and cleaned before disposal. It is not feasible to draw brine from selected wells in a given field, nor is it economic to continue pumping a well for its iodine after it has ceased to yield petroleum in paying amounts.

Methods of secondary recovery of petroleum probably benefit the iodine industry by prolonging the life of the

oil fields on which it depends. In the Dominguez field, where water-flooding is in progress, the iodine content of individual wells is watched. Although for a few wells it has declined, for the majority it has remained constant or increased. The increase may be caused by the washing out of precipitated salts.

The Dow Chemical Company operates iodine recovery plants at Seal Beach, Venice, and Inglewood; and the Deepwater Chemical Company Limited produces iodine at Dominguez Hill. A third company controls the right to extract iodine from the Long Beach field brine, but no iodine has been produced from it since 1934.

**Methods of Recovery.** The method of recovery used by the Dow Chemical Company resembles the blowing-out process for the recovery of bromine. Oil field waste water containing 62 to 67 parts per million of iodine is received in tanks, where it is clarified. The water is acidified, and chlorine gas is added to liberate the iodine. Iodine is removed from the water in a blowing-out tower, which consists of a vertical cylinder packed with rings made of ceramic material. The water containing free iodine enters the top of the tower where it meets a rising current of air. Iodine is carried by the air out of the top of the tower to a similar but smaller tower, where it is absorbed by a solution of  $\text{SO}_2$  in water according to the reaction  $\text{I}_2 + \text{SO}_2 + 2\text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4 + 2\text{HI}$ . The absorbing solution is maintained at a constant concentration of 1 pound of iodine per gallon by diluting it with fresh water and  $\text{SO}_2$ . Periodically some is drawn off and sent to the finishing department. All the iodine is finished at the Seal Beach plant, and the concentrated iodine-bearing liquor produced at Inglewood and Venice is transported there. In the finishing department the iodine is again liberated with chlorine, and the concentration is now high enough to permit the recovery of iodine by filtration. This product is purified by treatment with hot concentrated sulfuric acid and then dried. Material thus produced is crude iodine, 99.8 percent pure. Much of it is sold to chemical manufacturers for refining or the preparation of iodine compounds, but a portion is made into refined potassium iodide at the Seal Beach plant.

The Deepwater Chemical Company<sup>1</sup> uses the silver process for recovering iodine. Waste brine from oil wells of the Dominguez field is collected in a sump at the plant, which is north of Victoria Street, Compton. The iodine content averages 72 parts per million. Oil and floating debris are skimmed off before the brine is further cleaned by a flotation process. The cleaned brine is reacted with a measured amount of silver nitrate in one of three batch tanks. Insoluble silver iodide forms, and after the reaction is complete, ferric chloride is added to coagulate the precipitate and aid in its settling. The liquor is then decanted through a sand filter to recover any silver iodide that does not settle, and the silver iodide sludge is purified with boiling sulfuric acid. Soluble hydrocarbons are removed, ferric com-

<sup>1</sup> Girvin, C. W., and Witmer, E. B., 1950, The production of iodine in the United States: Unpublished paper presented before Am. Inst. Min. Met. Eng., Industrial Minerals Div., Los Angeles, Oct. 1950.



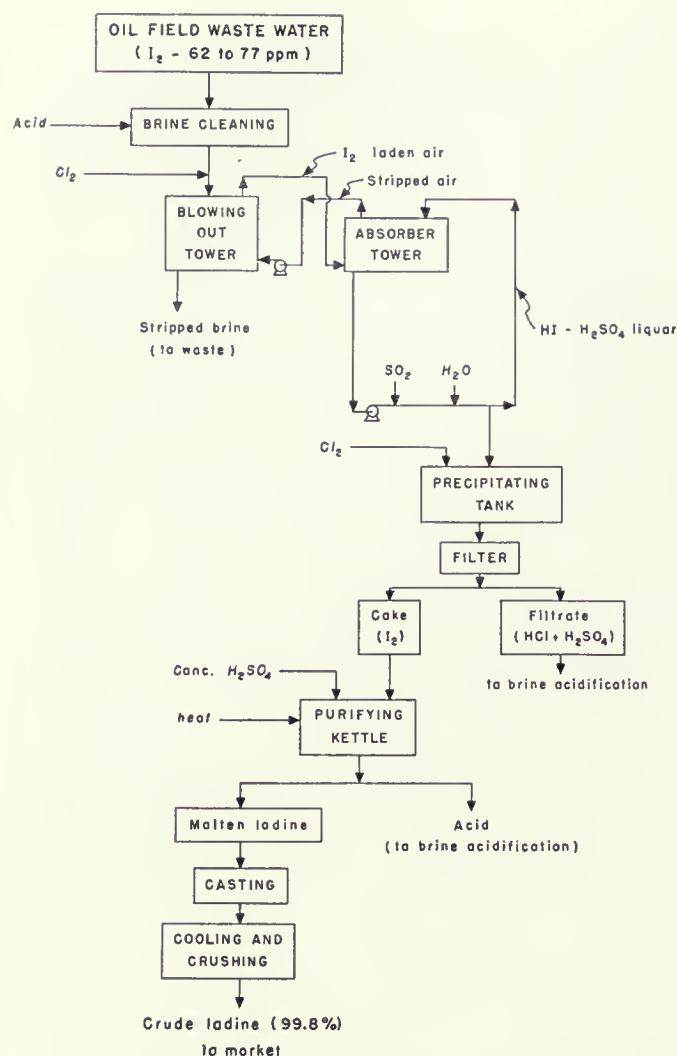


FIGURE 1. Flow sheet showing production of iodine from oil field waste water by the blowing-out process.

pounds are changed to soluble salts, and the silver iodide becomes a granular material with improved filtering properties. The silver iodide is recovered with vacuum filters and roasted to remove remaining traces of hydrocarbons.

The next step consists of recovering the silver for re-use. The silver iodide is tumbled with water and iron in a revolving cylinder. The iron reacts with the silver iodide, forming a concentrated solution of ferrous iodide and liberating metallic silver. Recovery of silver is high.

At one time the Deepwater Chemical Company produced free iodine from the ferrous iodide solution, but today potassium iodide of U.S.P. grade is recovered from it by treatment with potassium carbonate. To avoid contaminating the product, stainless steel equipment is used from this point in the process. The ferrous carbonate that precipitates is filtered out, and the potassium iodide is concentrated by evaporation. Further evaporation yields crystals of pure potassium iodide. Finally the crystals are dried in ovens, and packed in drums. A comparatively small amount of crude iodine is produced by treating old mother liquor with chlorine.

*Uses and Marketing.* Iodine and its compounds are valued for their antiseptic properties. Iodine is an essential element for humans and animals, and certain of its salts are sensitive to light. Its uses are limited by its relatively high price.

The United States consumed 1,173,874 pounds of iodine in 1952. Because only two companies produce iodine in the United States, the domestic production has not been disclosed in recent years; but it is a substantial portion of the consumption. In 1952 the crude iodine imported to the United States totaled 791,208 pounds, but imports are erratic and cannot be readily correlated with current consumption. Chile is the principal source

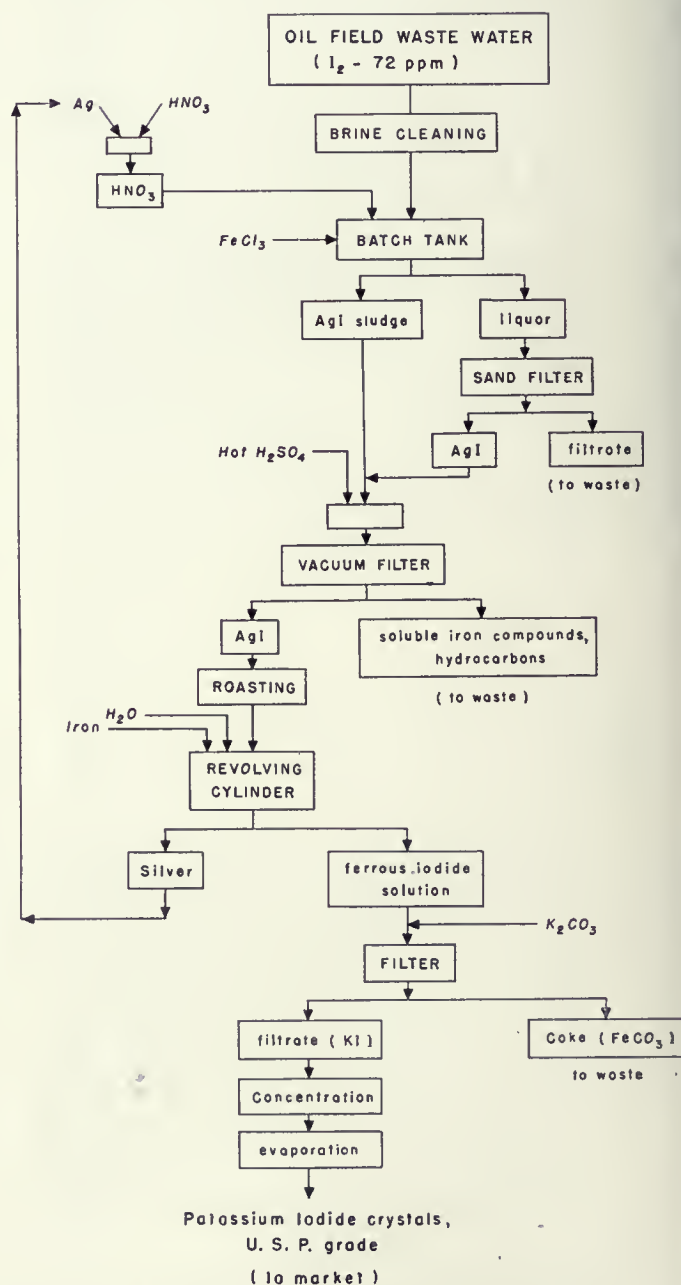


FIGURE 2. Flow sheet showing the production of potassium iodide from oil field waste water by the silver process.



of imported iodine, but since World War II imports from Japan have increased substantially.

Almost all the crude iodine produced in California as well as that imported into the United States is processed before use. Crude iodine is used approximately as follows:

Resublimed iodine-----	7 percent
Potassium iodide-----	65 percent
Sodium iodide-----	5 percent
Other inorganic compounds-----	3 percent
Organic compounds-----	20 percent

None of the processing plants are in California, and the crude iodine produced in California is shipped out of the state. A portion of the refined potassium iodide produced in California is marketed in the state, principally as additives to animal feeds and to salt for both table and animal use. For the United States as a whole the principal use of iodine compounds is probably for pharmaceutical purposes, and smaller amounts are consumed in the preparation of photographic materials and as laboratory reagents. Photographic uses have declined in importance because of technologic changes in the photographic industry.

According to the Oil, Paint, and Drug Reporter, the price of crude iodine in 1955 was \$1.45 a pound. The price of resublimed iodine was \$2.30-\$2.32 a pound and of potassium iodide, \$1.90-\$1.95 a pound except during March, April, and May when they were somewhat higher. The prices in California are approximately the same.

*History of Production.* The iodine industry is comparatively young. It was not until 1811 that Bernard Courtois, a French manufacturer of chemicals, discovered iodine in seaweed ash from which alkali had been extracted. In the early part of the nineteenth century iodine was produced with other salts from seaweed in Scotland and France, and today there is still some production from seaweed in Europe.

Today the most important source is the caliche of Chile, from which iodine is obtained as a byproduct of the nitrate industry. The Chilean industry, established in 1874, soon acquired a world monopoly, and by 1946 produced about 75 percent of the world's requirements. Assuming normal production of nitrate, Chile could, by the most conservative estimate, produce the entire world's consumption of iodine.

For many years prior to 1930 the price of crude iodine had been fixed at about \$4.00 a pound. Although using about 30 percent of the world's output, the United States produced very little iodine before this time. The

only exception was a few pounds produced with other chemicals from seaweed by an experimental plant operated in southern California in 1917. In 1928 the Dow Chemical Company which had been studying methods of recovering iodine from brine began producing iodine near Shreveport, Louisiana. Soon after, the General Salt Company began production at Long Beach, California, and was followed by the Deepwater Chemical Company. The Dow Chemical Company also built plants in southern California and abandoned the Shreveport operation in 1933. The General Salt Company ceased production in 1934.

The developments of the American iodine industry and later of the Japanese iodine industry have had a marked effect on the price of crude iodine. When the American production became significant, the price fell sharply and reached 81 cents a pound in October 1936. Crude iodine is imported duty free, yet the American industry was able to establish itself. The price soon rose to about \$1.00 a pound and was fixed at \$1.28½ during World War II. Following the war it increased gradually and reached as much as \$2.04 at times during 1951 and 1952.

In Japan the dormant iodine industry was revived during World War II in the interest of national self-sufficiency, and following the war she had an exportable surplus. Beginning in 1948, an increasing proportion of the iodine imported into the United States has come from Japan; in 1952 Japanese imports amounted to about 40 percent of the total. The price of crude iodine declined and was as low as \$1.15 during much of 1954.

The competition for the iodine market has resulted in a program of research and education, the purpose of which is to increase the use of iodine.

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## IRON INDUSTRIES \*

(Iron, Steel, Ferroalloys, Coke, Blast Furnace Slag)

By THOMAS E. GAY, JR.

Prior to establishment of the Kaiser Steel Corporation operation at Fontana, San Bernardino County, in 1942, California's iron industry consisted mainly of the manufacture of iron and steel products from scrap, pig iron, and iron ore brought into the state. Except for two relatively minor and short-lived blast furnace operations in Placer and Shasta Counties prior to World War I, the iron and steel plants in California had used little or no iron ore from deposits in California. The Kaiser Steel Corporation completed its first blast furnace in 1942, added a second in 1949, and a third in 1953, to increase its capacity to more than 1,300,000 tons of hot metal per year. In 1956, Kaiser Steel was the only California consumer of blast furnace ore. The Vulcan mine, in San Bernardino County supplied ore for the Kaiser blast furnaces until 1948, when the Eagle Mountain deposit in Riverside County was placed in production. Since 1948, the latter deposit has supplied the Kaiser plant's requirements for blast furnace ore, and, except for the Iron Mountain (Silver Lake district) deposit from which 20,000 tons were mined in 1953, has been the state's only source of ore for this use.

Most of Kaiser Steel's output of hot metal is converted to steel in the integrated steel plant at Fontana. All of California's other major steel plants—five in the Los Angeles area, and four in the San Francisco area in 1957—use scrap metal, or cold pig iron, the latter almost entirely from out-of-state sources, as their basic raw material. Scrap iron and scrap steel are necessary ingredients in the steel furnace charge of most California steel producers; scrap is substituted for pig iron in various proportions depending on their current relative costs.

The Kaiser Steel plant was founded mainly to supply ship plate to the west coast's World War II shipbuilding industry, but since the war, like the rest of California's steel industry, it has expanded and diversified.

California's iron industry includes several closely related components, which will be discussed in this section: (1) the iron-ore industry; (2) the steel-producing industry; (3) the ferroalloy industry; (4) the coke-producing industry; and (5) the blast-furnace slag industry.

Iron ore also has been mined in California for use in high-iron cement, in ferroalloys, as lump ore in steel furnaces, as heavy aggregate, as ship ballast and as paint pigment (table 1). The principal sources of iron ore for cement are the Vulcan, Cave Canyon, Bessemer, and Morris Lode deposits, all in San Bernardino County. Nearly all the iron ore used in making ferroalloys came from the Shasta and California deposits in Shasta County. Steel furnace lump ore has been obtained from the Bessemer, Iron Mountain (Silver Lake), Iron Age, and Amboy deposits, all in San Bernardino County. Most of the iron ore used for heavy aggregate and ship ballast, has come from the Shasta and California, Aptos Beach (Santa Cruz County), Eagle Mountain, and Bessemer deposits.

## IRON

*Mineralogy and General Geology.* The principal iron ore minerals are hematite ( $\text{Fe}_2\text{O}_3$ ); magnetite ( $\text{FeO} \cdot \text{Fe}_2\text{O}_3$ ); and limonite [ $\text{FeO}(\text{OH}) \cdot n(\text{H}_2\text{O})$ ] which, with other hydrous oxides, forms what is known commercially as "brown ore." Siderite ( $\text{FeCO}_3$ ) does not occur in commercial quantities in the United States. Pyrite ( $\text{FeS}_2$ ), one of the commonest iron-bearing minerals, is undesirable as an ore of iron because of its high sulfur content. Hematite, the most abundant iron ore mineral, contains 69.9 percent iron, and occurs both in a black, hard crystalline form, and a red soft, earthy form.

Magnetite, a black, heavy mineral (specific gravity about 5.2) with 72.4 percent iron content is characterized by strong natural magnetism. Limonite ores are mineralogically complex and commonly contain earthy admixtures which reduce the iron content appreciably below the ideal 57 to 66 percent range. Brown ores range in hardness from 1 to 5 on Mohs' scale and commonly have a yellow (ocherous) color.

Taconite is a hard, siliceous sedimentary rock that is especially abundant in the Mesabi Range in the Lake Superior region. It contains 25 to 30 percent iron, mostly disseminated as oxides, silicates, and carbonates. The first commercial production of iron from taconite ores began in 1956, after nearly a decade of intensive research and experiment to develop an economically successful process.

Most of the world's iron output has been obtained from deposits of three general modes of origin: (1) magmatic deposits, or those that have crystallized from magmas to form large irregular masses or veins; (2) sedimentary deposits, in which iron minerals and siliceous materials appear to have been simultaneously precipitated in subaqueous environments; and (3) residual deposits, which have been developed from the weathering of sedimentary deposits. The ore bodies of magmatic origin are characterized by predominance of magnetite, although hematite commonly has formed from post-magmatic processes. Magmatic deposits, although commonly higher grade, are less numerous, and commonly smaller than sedimentary or residual deposits. Among the largest and most productive magmatic deposits in the world are the high-grade magnetite ore bodies near Kiruna, Sweden. Among the most productive magmatic deposits in the United States are the magnetite ores of the Adirondacks, New York.

Sedimentary deposits commonly contain hematite and/or limonite, and less commonly siderite. The Clinton ores mined from New York to Alabama are among the most extensive and productive examples of this type.

Residual deposits commonly contain hematite or limonite. Some of the largest and richest deposits of this type are the hematite bodies of the Lake Superior region, which have yielded about 80 percent of the iron ore used in the United States. The most productive area in this district is the Mesabi Range.

\* Partly extracted from a section by James W. Vernon, in California Division of Mines Bulletin 156, 1950.





FIGURE 1.



Table 1. Summary of data on major California iron deposits.†

County	Deposit	Geology of deposit	Predominant ore mineral	Production			Estimated reserves	
				Date	Tons	Use	Grade (% Fe)	Long tons
Riverside	Eagle Mountain	Selective replacement of dolomitic beds in metamorphic series; related to quartz monzonite intrusion.	Hematite	1945 1948-mid 1956	40,000 9,800,000	Ship ballast Blast furnace	50	43,000,000
San Bernardino	Lava Bed district: Bessemer (Iron Mountain)	Many small contact-metamorphic and replacement bodies near dolomite-granodiorite contact.	Magnetite	1945 1951 1951	2,000 10,000 16,000	Foundries, ballast To Japan Cement	30-65	1,800,000
San Bernardino	Lava Bed district: Morris Lode	Similar to deposits in Bessemer area (above).	Magnetite	1949-1950	17,500		40	1,750,000
San Bernardino	Silver Lake district: Iron Mtn.	Contact-metamorphic replacement ore; brecciated and displaced by faulting to form lenses of fragmental ore intercalated in limestone breccia.	Magnetite	1953 1953	50,000 20,000	Steel (lump ore) Blast furnace	54	6,175,000
San Bernardino	Silver Lake district: Iron King	Elongated contact-metamorphic replacement bodies in quartzite and limestone intruded by monzonite.	Magnetite	None	--	--	--	375,000
San Bernardino	Old Dad Mountain	Vertical vein-like bodies in syenitic rock.	Magnetite	None	--	--	52-57	450,000
San Bernardino	Iron Age	Steeply inclined contact-metamorphic replacement bodies in limestone; partly in gneiss and quartzite.	Magnetite	1951 1956-1957	1,500 15,000	To Japan Steel (lump ore)	66	--
San Bernardino	Cave Canyon	Massive contact-metamorphic replacement bodies in limestone near monzonite contact.	Magnetite	1930-present	50,000 every 2 yrs.	Cement	60-67	3,500,000
San Bernardino	Vulcan	Contact-metamorphic replacement bodies in steeply dipping limestone near granite contact.	Magnetite	1942-1947 1951-present	2,643,000 35,000 every 2 yrs.	Blast furnace Cement	50	5,680,000
San Bernardino	Iron Hat (Ironclad)	Irregular lenses of brecciated hematite associated with chloritic schist, in brecciated granite and gneiss.	Magnetite & hematite	Undetermined	2,000	Iron works	57-59	185,000
San Bernardino	Ship Mountains	Vertically dipping tabular replacement bodies in pre-Cambrian limestone; apparently related to monzonite intrusion.	Hematite	1918	1,500	Iron works	61-66	80,000
San Bernardino	Kingston Range (Beck)	Elongate, flat-lying, layered lens in metamorphosed dacites and andesites intruded by a series of plutonic rocks.	Magnetite	None	--	--	60	Undetermined
Madera	Minarets	Discontinuous, shallow, replacement bodies and stringers in quartz diorite and Permian limestone and sediments.	Magnetite	None	--	--	60	5,000,000
Shasta	Hirz Mountain	Discontinuous, irregular contact-metamorphic lenses along contact of quartz diorite with Permian limestone.	Magnetite	None	--	--	--	260,000
Shasta	Shasta and California	Small, irregular hydrothermal replacement lenses in Carboniferous sediments, tuffs, and dolomite; genetically related to meta-diorite intrusion.	Magnetite	1907-1926 1942-1945 None	Undetermined 300,000 --	{ Pig iron Ferroalloys } Ship ballast --	38 30-60	4,680,000 175,000
Sierra	Lake Hawley—Spencer Lakes area	Black sand strata a few inches to several feet thick; interstratified with light sands on present beach and older terraces, from Pajaro River to Soquel Pt.	Magnetite	1926-1927 1944 (?)	5,000 10,000	Ferroalloys (experimental) Ship ballast	25-55	Undetermined
Santa Cruz*	Aptos Beach sand		Magnetite					

† Unless otherwise credited, data adapted from Lamey, et al., 1948.

\* Hubbard, H. G., 1943. Mines and mineral resources of Santa Cruz County: California Jour. Mines and Geology, vol. 39, pp. 35-36, 42-43.

† Wright, et al., 1953, p. 95; Hoffman, Maurice, personal communication, 1957.



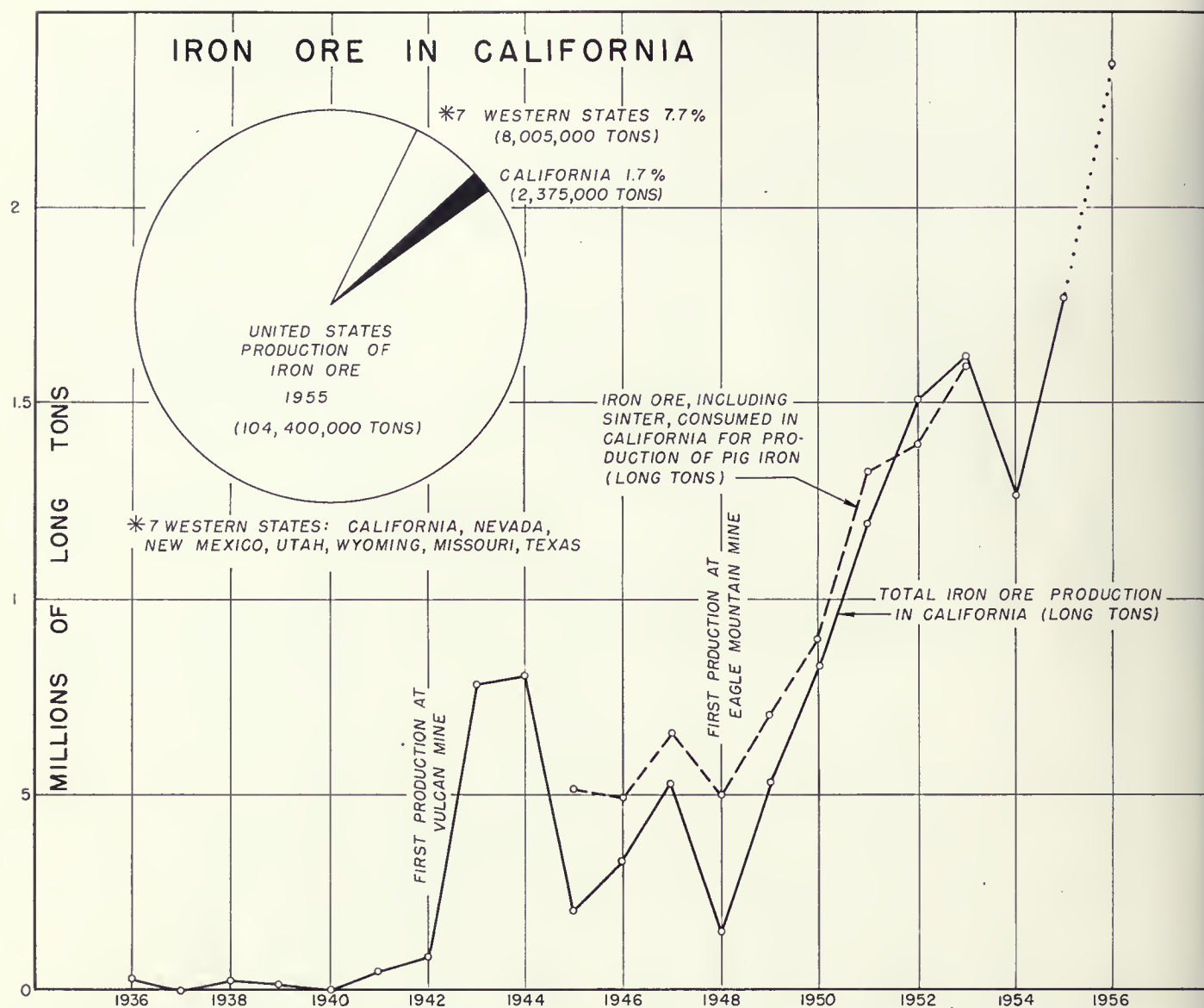


FIGURE 2. Production of usable iron ore containing less than 5 percent manganese in California, 1936 to 1956, and consumption of iron ore, including sinter, in California for production of pig iron, 1945 to 1953, both in long tons. (Data from U. S. Bur. Mines Minerals Yearbooks and Mineral Market Reports.)

Contact metamorphic deposits, such as occur in California, generally consist of magnetite and hematite, and have formed by replacement of carbonate rocks near contacts with granitic rocks. This type of deposit has yielded only a very small proportion of the world's iron ore. Whereas most of the major iron deposits of the world contain reserves that are measured in billions of tons, the Eagle Mountain deposit, by far the largest in California, has reserves measurable only in tens of millions of tons. No sedimentary or residual deposits of commercial interest have been noted in California.

*Localities in California.* Although hundreds of occurrences of iron ore minerals are known in California, production has been recorded from only about 30 deposits, of which eight have yielded more than 10,000 tons of ore, and only two more than one million tons. During World War II, 13 of the more important iron-bearing

localities in California were studied by the U. S. Geological Survey and the U. S. Bureau of Mines. Results of these investigations, including geologic maps and data obtained by trenching and drilling the deposits, were published in 1948 as Bulletin 129 of the California Division of Mines (Lamey, et al., 1948). Nine of these localities lie within an iron-bearing province in Riverside and San Bernardino Counties, southeastern California. Two other deposits are in Shasta County. Sierra and Madera Counties contain one each. Features of these deposits are briefly summarized in table 1. The deposits of Riverside, San Bernardino, and Shasta Counties are contact-metamorphic in origin and show the replacement of carbonate strata by iron-bearing minerals. The mineralization is genetically related to nearby intrusive rocks; the iron deposits ordinarily are at or near the intrusive contacts. In many places the mineralization was localized



by the intrusive contact, but control by faulting and fracturing in the intruded rocks is also common.

The Eagle Mountain iron deposits, the largest known in California, are in Riverside County 60 miles east of Indio (Hadley, 1949, pp. 1-24; McMillan, 1943). They are interlayered with a series of complexly folded and faulted metasedimentary rocks and are genetically related to sill-like masses of quartz monzonite which intrude the series. The ore bodies have formed mainly by the replacement of dolomite by magnetite. Five major ore bodies occur in a mineralized zone more than 6 miles long and about a quarter of a mile wide. They are 600 to 1,500 feet long, 70 to 300 feet thick, and extend 200 to 750 feet down dip (Lamey, et al., 1948, p. 3). Much of the magnetite has been altered to hematite. Pyrite, which averages about 3 percent in fresh ore, has generally been removed by oxidation to an average depth of 200 feet. The ore mined for blast-furnace feed averaged about 52.5 percent iron until 1954 when a beneficiation plant was installed to raise the average grade to about 55 percent iron.

The Vulcan deposit, 9 miles southeast of Kelso, northeastern San Bernardino County, consists of two orebodies; the exposure of the larger one is 700 feet long and 325 feet wide. The ore minerals are magnetite and

hematite, with limonite present locally. The orebodies are replacements of limestone and lie near a limestone-monzonite contact (Lamey, et al., 1948, p. 90).

All of the other major iron deposits in the southern California area are in San Bernardino County, and include the Bessemer (Iron Mountain) and Morris Lode deposits (Lava Beds district), about 26 miles southeast of Daggett; the Iron Mountain and Iron King deposits (Silver Lake district) about 15 miles northwest of Baker; the Old Dad Mountain deposit, about 20 miles southeast of Baker; the Iron Hat (Ironclad) deposits about 6 miles north of Cadiz; the Ship Mountains deposit, about 3 miles east of Siam; and the Kingston Range (Beck) deposits, about 37 miles northeast of Baker. The ore minerals at all these deposits consist of magnetite with subordinate hematite, and minor limonite. The grade of most of these deposits ranges from less than 30 to more than 60 percent iron. The detrimental impurities phosphorus and sulfur are present, but within commercial limits, in most of the orebodies of these deposits.

The California, Shasta, and Hirs Mountain iron deposits in Shasta County also are contact-metamorphic replacements of calcareous sediments associated with granitic intrusive rocks.

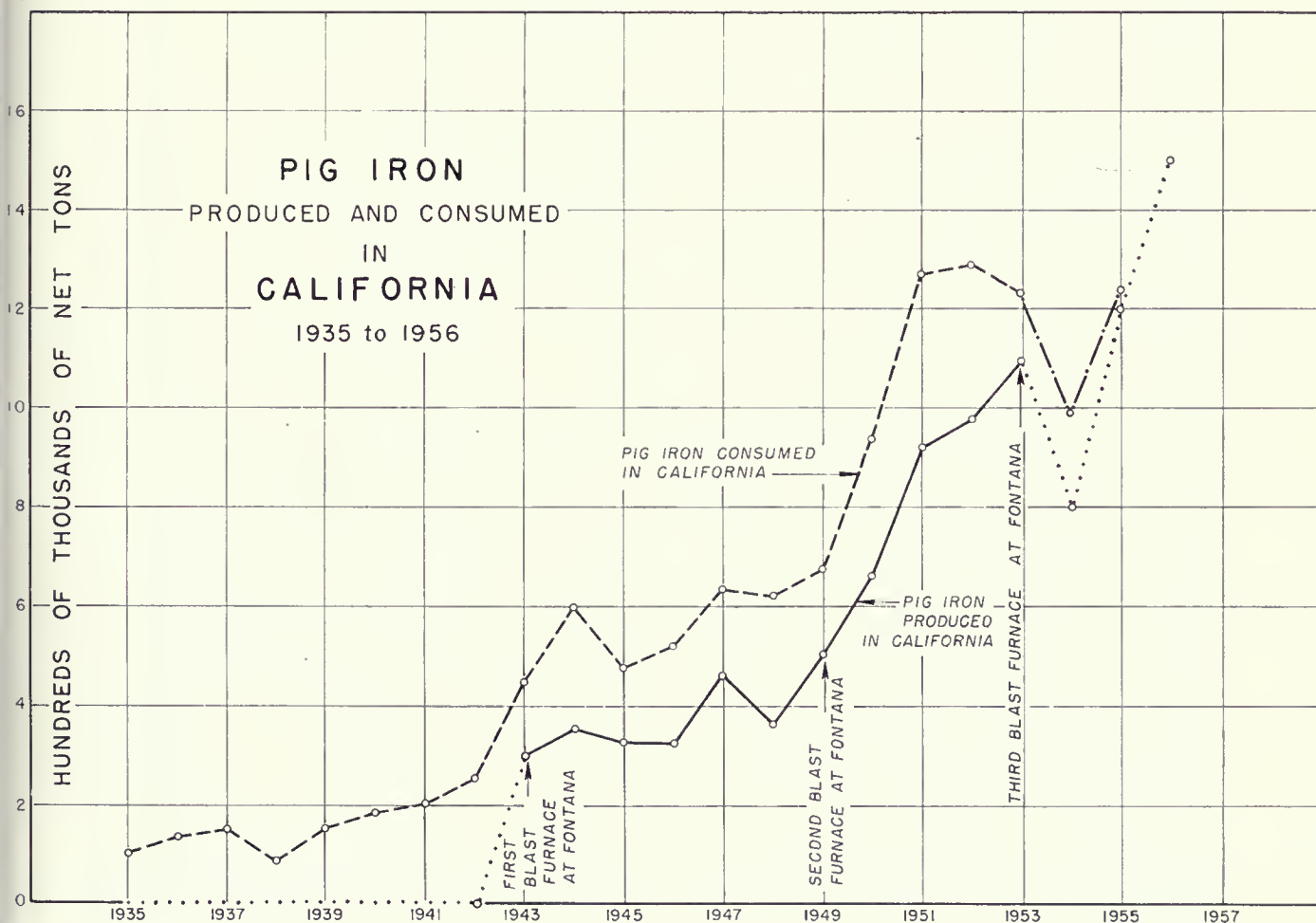


FIGURE 3.



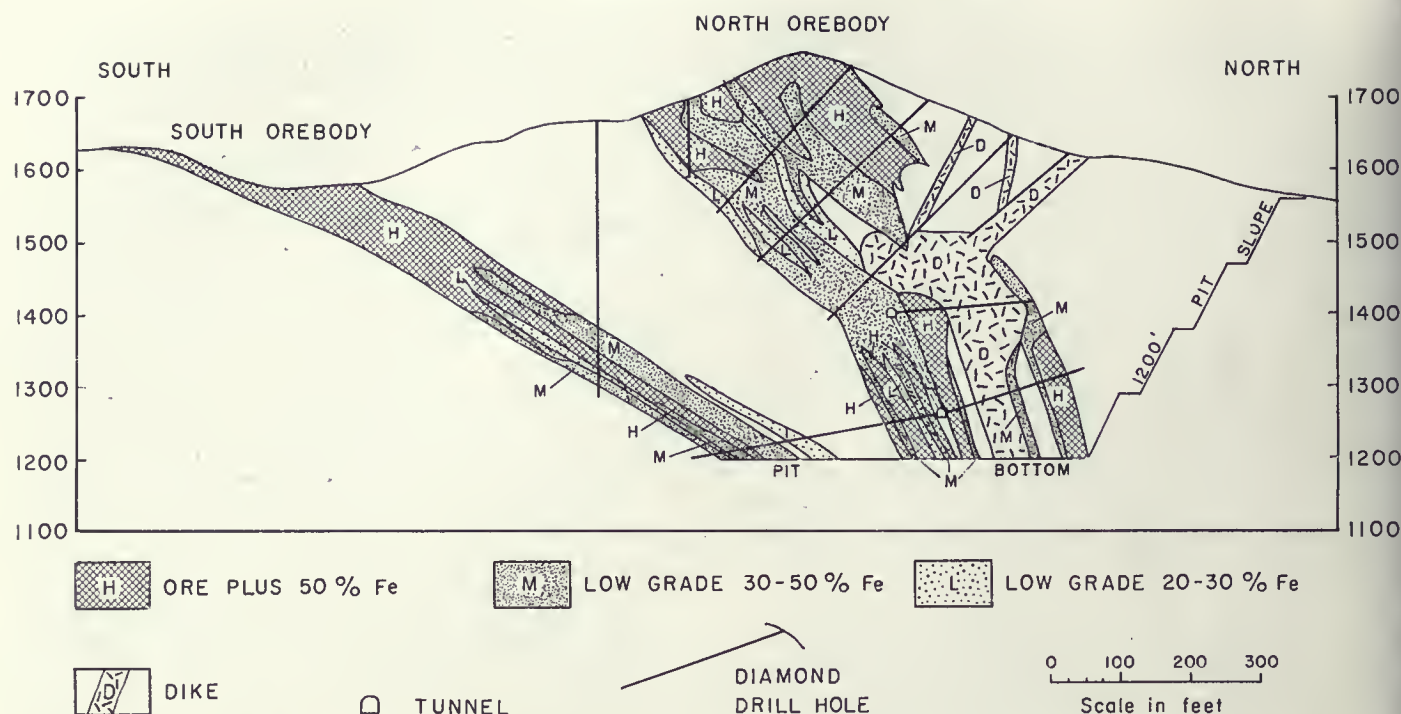


FIGURE 4. Section through North and South orebodies, Eagle Mountain iron mine, Riverside County, California. Two ore-bearing calcareous beds, 40 to 80 and 90 to 400 feet wide, are separated by 50 to 250 feet of quartzite. Section shown is near east end of broad, east-trending anticline, whose crest and south limb have been removed by erosion. (Section and data courtesy of K. B. Powell, Superintendent of Raw Materials, Kaiser Steel Corporation.)

Iron deposits in Sierra County near Lake Hawley and Spencer Lakes are magnetite replacements of clastic sediments, tuffs, and lamprophyre dikes. The magnetite is probably genetically related to nearby bodies of meta-diorite. These deposits have been dynamothermally metamorphosed. The Minarets deposits of Madera County are flat-lying magnetite-rich lenses in a sequence of metamorphosed volcanic rocks. Sedimentary and magmatic iron deposits are uncommon in California.

**Reserves.** Iron ore reserves of California have been conservatively estimated at 100 to 150 million tons, of which about half is considered to be sub-marginal under present economic conditions (Lamey, et al., 1948, p. x). The nine largest deposits of southeastern California contain approximately three-fourths of the known reserves. The Eagle Mountain deposits alone contain at least one-third of the total known reserves. These deposits were estimated in 1948 to contain 28,000,000 tons of measurable ore assaying 30 percent iron or more; an additional 15,000,000 tons containing 45 to 50 percent iron was inferred (Lamey, et al., 1948, pp. 12, 13). Subsequent exploration has increased the known reserves of the deposits so that at the present rate of mining ( $1\frac{1}{2}$  to 2 million tons of ore per year), ore for 25 years operation of the Fontana plant has been proved (Powell 1953).

**History.** The first iron foundries and forges on the west coast were built in San Francisco to meet the demand for iron and steel products in the years during and following the Gold Rush of 1849. The raw material for these early operations was mainly scrap iron from railroad and mine machinery brought by sailing vessels around the Horn. Nearly a score of California iron deposits reported production before World War II, but

their output of iron ore was discontinuous and relatively minor. Except for two small-scale pig iron-producing operations, at Hotaling, Placer County, and Heroult, Shasta County, almost all of the iron ore produced in California before World War II was used as a minor ingredient in local steel and iron works.

No output of iron ore in California was recorded before 1880, when the California Iron Works blast furnace was built near Clipper Gap, Placer County (Logan 1927, p. 281). About 30 tons of high-quality pig iron was produced per day from ore mined at the nearby Hotaling mine; charcoal was used for fuel, and local limestone for flux. Most of the output was used for railroad car wheels and axles, but some was sold to other California iron works. In 1886, the operation closed because of competition from iron brought in as ship ballast, and depletion of reserves of high-grade ore. During the 6-year life of the operation, 30,736 tons of pig iron valued at \$263,991 were produced (Hodge 1935, appendix E-5, p. 3). From 1907 to 1914, the Noble Electric Steel Company produced high-quality pig iron in an electric furnace at Heroult, Shasta County, using ore from the nearby Shasta Iron Company deposit. The daily capacity of this operation was 25 tons of pig iron. Charcoal, quartz, and limestone from local sources were used in the furnace charge. After the World War started in 1914, the operation was converted to the production of ferromanganese and ferrosilicon, but post-war economic pressure forced it to close.

From World War I to World War II, California's iron and steel foundry industry continued to expand, diversify, and consolidate, to keep pace with the state's expanding industrial economy. California's iron and steel furnaces continued to be charged with out-of-state





FIGURE 5. Aerial photograph, view north, showing the Eagle Mountain iron mine of Kaiser Steel Corporation, near Desert Center, Riverside County. This mine yields more than 2,000,000 tons of ore per year for reduction in the Company's three blast furnaces at Fontana. At left are benched pit and waste dumps of Bald Eagle orebody, inactive since 1952. At left center are railroad car loading facilities and ore beneficiation plant. At right are pits and dumps of North and South orebodies, active since 1951. In left foreground are Company offices and shops; in right foreground are employees' living quarters. *Photo courtesy of Kaiser Steel Corporation.*





FIGURE 6. Iron ore beneficiation facilities at Kaiser Steel Corporation's Eagle Mountain mine, viewed westerly. More than 50 percent of the mine's output is beneficiated by magnetic and heavy-media processes, raising the average grade of all ore shipped to about 60 percent iron. Railroad car loading facilities, dumps of Bald Eagle pit, and portions of Eagle Mountains in right distance. *Photo courtesy of Kaiser Steel Corporation.*

pig iron and scrap until World War II when demands for increased steel production provided the stimulus for Kaiser Steel Corporation to produce iron from local iron ores. The Vulcan mine, near Kelso, San Bernardino County, was developed first largely because it was close to existing railroad transportation, whereas wartime material restrictions delayed construction of transportation facilities to the larger Eagle Mountain deposit in Riverside County. The Vulcan mine yielded a total of 2,643,000 tons of blast furnace ore from 1942 to 1948. Depletion of the easily mined reserves and high sulfur content in the deeper Vulcan ore were contributory reasons for its closing, and the opening of the Eagle Mountain mine, in 1948, as a continuing supply of blast furnace feed. From 1948 to mid-1956, more than 9 million tons of blast furnace ore have been produced at Eagle Mountain. In

1952-53 the Iron Mountain (Silver Lake) deposits, about 15 miles northwest of Baker, San Bernardino County, yielded about 20,000 tons of blast furnace ore, on a test basis, for Kaiser Steel Corporation. Demand for iron ore for export to Japan led to production of about 16,000 tons from the Bessemer mine, about 26 miles southeast of Daggett, and about 3,400 tons from the Iron Age mine, 22 miles east of Twentynine Palms, San Bernardino County, in 1951.

*Notable events in the history of California's iron industry*

<i>Year</i>	<i>Event</i>
1849	Union Iron Works, San Francisco, produced first casting made in California. Vulcan Iron Works, Miner's Foundry, Pacific Iron Works reported active.
1868	Pacific Rolling Mills, San Francisco, produced first hot-rolled iron bars, using railroad scrap (largely from England) and coal from Australia.



- 1880 First California iron ore produced at Hotaling mine, Placer County, and converted to pig iron in local blast furnace, using charcoal (1880-86).
- 1881 First steel rolled in California from steel blooms brought from Europe.
- 1884 Pacific Rolling Mills, San Francisco, produced first heat of steel made in California, from English pig iron, Spanish iron ore, and local scrap.
- 1888-93 Union Iron Works, San Francisco, built cruisers Charleston, Olympic, San Francisco, and battleships Wisconsin, and Oregon.
- 1907-14 Noble Electric Steel Company produced pig iron in electric furnace at Heroult from ore mined at Shasta Iron Company mine; produced ferroalloys in same furnace from 1914 to 1917.
- 1942 Kaiser Steel Corporation established integrated steel plant at Fontana, with first modern blast furnaces. Used ore from Vulcan mine, San Bernardino County, for blast furnace feed.
- 1948 Kaiser Steel Corporation shifted mining operation from Vulcan mine to Eagle Mountain mine, Riverside County, California's only active source of blast furnace ore in 1956.

## Utilization

About 96 percent of the iron ore consumed in California is for blast furnace feed; about 3 percent is for low-heat cement and less than one percent is used as lump ore in steel furnaces. Pigment and ferroalloy manufacture, and ship ballast have utilized minor tonnages of iron ore in California. Iron ore also is used in heavy media, foundry sands, and drilling muds but a negligible amount of the iron ore mined in California is thus consumed.

**Blast Furnace Feed.** For use in blast furnaces, the iron content of ore should be at least 50 percent; the average natural content of all ore mined in the United States in 1953 was 50.36 percent Fe (Forbes 1956, p. 552); about 30 percent of this ore was beneficiated before use. As sulfur is a highly objectionable impurity, ores containing more than 0.1 percent are commonly unacceptable. Phosphorus should be less than 0.1 percent of the ore if the resultant iron is to be used for steel; as much as 2 percent is acceptable in ores for some of the rarely used types of iron. Ores that contain 0.045 percent phosphorus or less are classified "Bessemer"; those with 0.045 to 0.180 percent phosphorus as "non Bessemer" because the resulting iron cannot be converted to steel by the Bessemer process. Lime, alumina, silica, and magnesia in amounts of as much as several percent are

Table 2. Generalized specifications for desirable iron ore for blast furnace feed. From U. S. Bur. Mines, 1956, p. VII-3.

## A. Size analysis \* :

Screen size	Percent passing
2-inch	100
1-inch	70
$\frac{1}{2}$ -inch	not more than 20

\* Ideal ore would be uniform in size, about one-quarter-inch in diameter.

## B. Chemical composition :

Components	Percentage
Fe	50-55
Mn	0.8-1.5
SiO <sub>2</sub> + Al <sub>2</sub> O <sub>3</sub>	10 (max.)
CaO + MgO	(usually low)
P	0.18 (max.)
S	0.10 (max.)
Cu, Pb, Zn, As, V, Cr, Ni	0.05 (combined)
TiO <sub>2</sub>	1.0 (max.)
H <sub>2</sub> O	10 (max.)



FIGURE 7. Beck (Kingston Range) iron deposit, near Beck Spring, San Bernardino County. View westerly at Iron Gossam No. 5 claim, main outcrop of deposit. The dark colored, iron-bearing body (hillcrest, center) is 100 to 150 feet thick, and dips steeply between diabase (left) and limestone of the pre-Cambrian Crystal Spring formation. In foreground is dump and portal of 300-foot Beck exploration adit. Five diamond drill holes, drilled from left side of outcrops, penetrate the body shown.



FIGURE 8. Iron Mountain (Silver Lake) iron deposit, San Bernardino County, viewed westerly. Dark outcrops, with benches from 1952-1953 mining operation, are largely magnetite-rich breccia, in low-angle contact with brecciated dolomite and andesite, all of Tertiary (?) age. Rounded hills in left background are largely pre-Tertiary (?) igneous rocks; Quaternary alluvium and colluvium surrounds the visible iron-bearing outcrops.





FIGURE 9. Cave Canyon iron deposit near Afton Canyon, on southeast flank of Cave Mountain, San Bernardino County, viewed northwesterly. Dark areas in the open cut are remnants of magnetite- and hematite-rich, steeply inclined orebodies formed mainly by contact metamorphic replacement of limestone and dolomite associated with gneissic and quartzitic rocks, all possibly pre-Cambrian in age. Ore from this deposit is used in cement manufacture.

desirable impurities, as they have fluxing and slagging properties.

**Cement Manufacture.** The second largest market for California iron ore is in the manufacture of low-heat portland cement. Such cement, which contains about 5 percent iron oxide ( $\text{FeO}$ ) as a chemical ingredient, evolves 15 to 35 percent less heat of hydration during setting than do regular or high-early-strength cements (Shreve, 1945, pp. 190-191, 198-199). Low-heat cement is used in massive structures, such as dams, to minimize cracking of the structure from internal thermal stresses.

To make low-heat cement, iron-bearing substances are ground and added to the regular cement ingredients before they are fused to form clinker. Roll scale or pyrite cinders are the main sources of iron for the northern California producers of high-iron cement, and for about half of the producers in southern California. About 40,000 tons of iron ore are used each year for this purpose by southern California cement manufacturers. Iron present in laterite (iron- and alumina-rich residual clayey soil) mined in large tonnages near Ione, Amador County, primarily for its alumina content, provides a large share of one northern California cement manufacturer's requirements of iron for this purpose.

Although the specifications for iron ore for cement manufacture are not released by the manufacturers, high iron content is desirable. Most of the iron ore produced in California for this use contains 60 percent or more iron.

The principal sources of iron ore for cement manufacture are the Cave Canyon and Vulcan mines, which have supplied this market since about 1930 and 1951

Table 3. Iron ore consumed in California for the manufacture of high-iron cement, 1944-56. Data from U. S. Bureau of Mines Minerals Yearbooks, except as noted.

Year	Net tons	Year	Net tons
1956	42,500 <sup>1</sup>	1949	29,945
1955	42,500 <sup>1</sup>	1948	38,062
1954	42,500 <sup>1</sup>	1947	35,112
1953	43,484	1946	48,172
1952	44,579	1945	20,583
1951	39,242	1944	16,298
1950	33,881		

<sup>1</sup> Estimated.

respectively. Each property is worked for several months at approximately 2-year intervals, and 35,000 to 50,000 tons of ore is stockpiled. This supply lasts about 2 years, when another batch is mined. In 1949 and 1950, before the Vulcan mine output was put to use in cement manufacture, about 17,500 tons of iron ore was obtained from the Morris Lode mine for this use, as were about 10,000 tons from the Bessemer mine in 1951.

**Lump Ore in Steel Furnaces.** Relatively small tonnages of high-grade iron ore are used in open-hearth steel furnace charges to provide oxygen to oxidize carbon, silicon and phosphorus from the molten bath in the later stages of the steel-refining process. Iron ore may be used similarly in electric furnace manufacture of steel, but the tonnage of ore consumed in California in electric steel furnaces is negligible. Lump ore is thus named because it must be in hard, large pieces, generally between one and ten inches in diameter, with no fines. Maximum iron content is desirable, because high-iron ores are the densest and because such ores introduce fewer impurities while providing the most available oxygen per unit of volume. High silica content is undesirable in



Table 4. Specifications for iron ore (lump ore) used in open-hearth steel furnaces by three large steel-producing companies.

A. Size requirement:

	Consumer A	Consumer B	Consumer C
Maximum lump -----	12 in.	8 in.	10 in.
Minimum lump -----	1 in.	-	2 in.
Fines -----	less than 10% smaller than 1 inch.	Free of fines.	-

B. Chemical Composition (percent)

Iron (minimum) -----	65	60	65
Sulfur (maximum) -----	"low"	0.05	0.05
Phosphorus (maximum) -----	"low"	-	0.05
Silica (maximum) -----	"low"	5	5

lump ore for basic open-hearth furnace use because the siliceous slag that forms from such ores corrodes the furnace lining unless additional limestone is added.

Lump ore generally constitutes less than 5 percent of the charge of the open-hearth furnace. Oxygen supplied directly to the molten steel, and roll scale (which forms by surface flaking when steel is hot-rolled) are used in place of lump ore in many of California's open-hearth furnaces. Kaiser Steel Corporation brings in several thousand tons of lump ore from Utah each month for the nine open-hearth furnaces at Fontana. The total lump ore requirements of all other steel-making facilities in California are estimated to be less than 1,000 tons per month. Depending on quality, most lump ore used in California costs from 15 to 20 dollars per ton delivered; imported ore of exceptional quality has been sold here for as much as \$28 per ton.

The ore from most of the iron deposits in California contains too much sulfur for use as lump ore in steel furnaces. Selected ore from several mines, including the Iron Mountain mine (Silver Lake district), the Amboy deposits, about 4 miles northwest of Amboy, and the Iron Age mine, about 13 miles east of Dale Lake, all in San Bernardino County, has been used successfully, but most lump ore is brought into the state from deposits in Utah, Colorado, Nevada, Vancouver, B. C., and South America.

In 1952 and 1953, about 50,000 tons of lump ore was mined from the Iron Mountain mine for use by Kaiser Steel Corporation as part of a test program. In 1953, about 10,000 tons of ore that averaged 68 percent iron were mined at the Amboy mine, and shipped to Ohio where it was sold as lump ore for about \$22 per ton. Starting in November 1956, ore containing about 66 percent iron, 0.03 percent sulfur, and 0.06 to 0.07 percent phosphorus was mined at the Iron Age mine for sale to Kaiser Steel Corporation for use as lump ore, on a 15,000-ton, 6-month contract. About 50 tons per day of float and near-surface ore was mined and trucked 40 miles to Amboy, where it was sold for \$13 per ton, f.o.b. cars. A small tonnage of ore from the Hilltop mine, about 6 airline miles north of Trinity Center, Trinity County, was shipped to the Pacific States Steel Company at Niles in 1956. Minor tonnages have been mined during brief periods for this use at several California deposits in the past, but production data are not available.

**Ship Ballast and Heavy Aggregate.** Iron ore, because of its high specific gravity, has been used as an inexpensive material for the ballasting of ships, for counter-

balances for bascule bridges, as a weight in heavy rollers, and as shields in atomic reactors. Ore may be used either in its natural, broken state, as in the holds of ships, or as an aggregate in heavy concrete. Depending on the purity, magnetite and hematite ore (specific gravity about 5.3) weigh from about 250 pounds per cubic foot, for 50 percent ore, to about 330 pounds per cubic foot for 100 percent ore. Ordinary concrete weighs about 145 to 150 pounds per cubic foot, so an increase in specific weight of 50 to 85 percent is possible in concrete made with iron ore substituted for sand and gravel aggregate. For use as ship ballast, iron ore should weigh more than 210 pounds per cubic foot (L. W. O'Donnell, Bethlehem Pacific Coast Steel Corp., personal communication, 1953). Concrete weighing more than 250 pounds per cubic foot has been extensively used for permanent ballast in ships (ASTM 1956, p. 218). The ore should be compact and hard, and of maximum iron content—preferably more than 60 percent iron. Chemical impurities, other than those that might react with cement, are not detrimental.

During World War II, about 360,000 long tons of magnetite ore, of 4.5 specific gravity, were used as ballast in ships constructed on the Pacific Coast (Severy, 1948, p. 3), all in the form of heavy concrete. About 325,000 tons of iron ore were mined for this purpose in California from 1942 through 1945 (Severy 1948, p. 3). About 300,000 tons, averaging more than 67 percent iron, were obtained from the Shasta and California deposits; 2,000 tons from the Bessemer mine; 13,000 tons from the Eagle Mountain mine; and 10,000 tons of fine-grained beach magnetite from Aptos, Santa Cruz County. The most recent reported production of California iron ore for use as heavy aggregate was in 1948 at the Shasta and California deposits. This ore, which contained a minimum of 58 percent iron, and had a specific gravity of not less than 4.5 was valued at \$8 per net ton, f.o.b. cars, Redding. Since 1953, several thousand tons of iron ore mined in Nevada have been consumed in California as heavy aggregate. An undetermined but small tonnage of titaniferous magnetite from Hermosa Beach and Sand Canyon, Los Angeles County, has been used locally to make heavy concrete.

**Paint Pigment.** In their finely divided state, iron ore minerals have long been used as natural pigments, or mineral paint, for their yellow, brown, and red colors. Hematite has a characteristic red color and the hydrous oxide limonite is yellow; these colors may be modified by calcination, or by admixture of other substances. The earthy, commonly impure, natural mixture that consists mainly of clay permeated with hydrous iron oxides is called ocher. A yellow color is characteristic, but reddish hues occur where hematite is present or when the ocher is calcined.

The use of natural pigments has declined in recent years, while synthetic pigments have become more and more widely used. The principal use of natural iron pigments is in paint for relatively non-exacting purposes, such as for freight cars, barns, roofs, and industrial applications where slight color variation is permissible, and low cost is desirable.

The following factors have influenced the trend away from natural pigments: (1) a greater number and va-





FIGURE 10. The three blast furnaces at Kaiser Steel Corporation's Fontana plant, San Bernardino County. The three tank-like structures from which pipes lead upwards to the blast furnaces cleanse the gases resulting from the burning of coke in the furnaces, for use in the coke plant. Railroad cars (right) are removing slag; horizontal tank-like railroad cars, barely visible beneath spectators, will carry molten iron to open hearth furnaces for conversion to steel. *Photo courtesy of Kaiser Steel Corporation.*

riety of colors are available in synthetic pigments than in natural pigments; (2) closer control can be maintained over the quality of synthetic pigments than of natural pigments; (3) color, and other characteristics, tend to vary from place to place within a given deposit of natural pigment; and (4) synthetic pigments are more convenient to transport, handle, and process than are most natural pigments. The low cost of natural iron pigment (about 3 or 4 cents per pound compared to about 30 cents for synthetic pigment) is its principal competitive advantage.

For use as pigment, iron ore materials should have a hardness of less than 5, to permit fine grinding; should be uniform in color; should contain 50 to 90 percent iron oxide, with little or no silica, alumina, or lime; and should contain no sulfur, zinc, or copper. The deposit should be large enough to ensure a continuing supply of similar pigment for a number of years.

Since 1950, the consumption of natural iron oxide for manufacture of paint pigment in California has been about 500 tons per year, all processed by one firm, C. K. Williams and Company, in Emeryville, Alameda County (E. G. Ratcliffe, personal communication, 1956). The raw material is mainly limonite, obtained from Oregon, and delivered, crude, in Emeryville for \$20 to \$25 per ton.

More than 50 deposits of iron oxide mineral pigment, of varied quality and quantity, have been reported in California. These are distributed in 24 counties (Symons

1930). Minor tonnages of pigment have been obtained from most of these deposits, mainly for local usage. Shipments of 25,933 tons of pigment, valued at \$249,038, have been reported from more than a score of deposits, in 14 counties, during the period 1890 to 1946 (Averill, et al., 1948, p. 82).

Since 1946, the only production of mineral paint in California has come from two deposits: one near Ludlow, San Bernardino County, which yielded undetermined but small tonnages in 1947, 1948, and 1949; and the Leona Heights deposits in Alameda County which yielded a small tonnage in 1951.

**Ferroalloys.** Where necessary in the manufacture of ferroalloys, such as ferrosilicon, iron may be introduced in the form of metallic iron (pig, scrap, or cuttings), or as oxide ore. Modern practice favors the use of metallic iron rather than iron ore for this purpose. The three firms that have produced ferroalloys in California, are all now defunct. Only the Noble Electric Steel Company operation, at Heroult, Shasta County, used iron ore. This firm utilized an undetermined tonnage of iron ore, from the nearby Shasta and California deposits, to make ferromanganese, ferrosilicon, silicomanganese, and ferrochromium during World War I. The ore contained 68 percent Fe, and negligible amounts of sulfur and phosphorus.

The Pacific Electro Metals Company (later the Pacific Alloy and Steel Company), active during World War I



at Bay Point, Contra Costa County, utilized metallic iron in the form of cuttings to make silico-manganese and ferromanganese. The state's principal and most recently active producer of ferroalloys, the Permanente Metals Corporation (now Kaiser Aluminum and Chemical Corporation), also used metallic iron in the form of scrap cuttings at its Permanente plant, Santa Clara County, to make ferrosilicon.

**Heavy Media.** In the heavy-media process of ore separation (American Cyanamid Co., 1953) finely ground heavy material is suspended in water to form a "heavy media" with liquid characteristics. The specific gravity of the resulting medium is maintained midway between that of the ore and the gangue minerals to be separated, so that one floats and the other one sinks. Specific gravity of the medium may be controlled within 0.01 of the optimum specific gravity for separation of a given ore and gangue.

Magnetite, and ferrosilicon (85 percent iron and 15 percent silicon) are the heavy media most widely used,

because they are easily recovered and cleaned by magnetic means, relatively low in cost, readily available, resistant to abrasion and chemical action, and able to form fluid media over a wide range of specific gravities (1.25 to 3.40). In 1956, three mineral beneficiating operations in California were using the heavy-media process; ferrosilicon was the heavy medium used at all three operations. Kaiser Steel Corporation was using heavy media at Eagle Mountain mine to beneficiate iron ore; Kaiser Aluminum and Chemical Corporation was beneficiating dolomite at Natividad, Monterey County; and Southern Pacific Milling Company was beneficiating sand and gravel for aggregate at Santa Maria, Santa Barbara County.

Magnetite is prepared as heavy media in several eastern states and abroad. Three grades of heavy media magnetite are sold by a large producer in Pennsylvania; all cost \$40 to \$45 per ton delivered in California. Grade "A" is about 60 percent minus 325 mesh in size, grade "B" about 90 percent minus 325 mesh, and grade "C" about 45 percent minus 325 mesh.



FIGURE 11. Casting operation at one of the 1200-ton blast furnaces of Kaiser Steel Corporation's Fontana plant. Molten iron flows through the runner (bottom right) to a ladle car while the impurity-laden, lighter slag, which floats on the iron, is skimmed off and directed through the more distant runner into slag pits to the right of this picture. Approximately 300 tons of molten iron are drawn from each of the three blast furnaces five times each day. *Photo courtesy of Kaiser Steel Corporation.*



**Foundry Sands.** Finely ground hematite is mixed in small quantities with foundry sand at many California ferrous metal foundries. The hematite is used, particularly in cores, to lower the fusion temperature in the sand, thereby increasing its plasticity and decreasing the danger of distortions due to expansion of the core when the casting is poured. The California foundry industry consumes an estimated 100 tons of hematite per year for this purpose. Its delivered cost is about \$70 per ton. The pulverized hematite used in foundry sands is practically identical in size and composition with iron ore used for pigments. In California, both products are manufactured from out-of-state raw materials by the same producer.

Magnetite sand, graded in the size range of ordinary foundry sand, has been used experimentally in aluminum casting practice to avoid uneven solidification. The high density and high specific heat of the magnetite grains enable the heat from the poured metal to be absorbed and transmitted rapidly, thus avoiding the stresses set up in the metal during uneven solidification. Zircon sand has been most commonly used for this purpose (see section on special sands in this volume), but recent increases in the cost of zircon sand may lead to its partial replacement by magnetite sand for this use. Zircon sand sold for about \$75 per ton in 1956, compared to an approximate cost for magnetite sand of \$5 to \$10 per ton.

**Drilling Mud.** Finely ground iron ore, principally hematite, was commonly used, prior to 1930, in oil well drilling muds, to increase the specific gravity of the mud. Barite, which is more economical to produce in ground form, and more consistent in its specific gravity, has completely replaced iron ore in this use.

#### Marketing of Iron Ore

In 1956, virtually no open market existed in California for the two classes of iron ore consumed in greatest quantity in California: blast furnace ore, and ore used in the manufacture of low-heat cement. Company-owned or leased mines fulfilled the requirements for these types of ore at costs generally lower than could be met by independent operators. For example, in 1955 blast furnace ore containing 55 percent Fe was mined at Eagle Mountain mine and delivered at Fontana, for a total cost of about \$2.50 per net ton, or well below known competitive prices. The offered price of about \$10 per long ton for 60 percent ore loaded aboard ship for export to Japan, led to a small production from the Bessemer and Iron Age mines in 1951. Although production difficulties soon led to the closing of these operations, iron ore mined in Nevada continued to be shipped to Japan through California ports in 1956.

The demand for limited tonnages of high-grade lump ore for steel furnace use has increased since 1950, both for local and out-of-state markets. The Iron Age and Iron Mountain (Silver Lake District) deposits have yielded ore for this market at times since 1950, and other relatively small but high grade deposits may be worked for this market. Projected expansion in California's present steel-making capacity will almost certainly increase the demand for lump ore.

Since prior to 1950, the demand has been too slight to make profitable the mining of iron ore for use as heavy

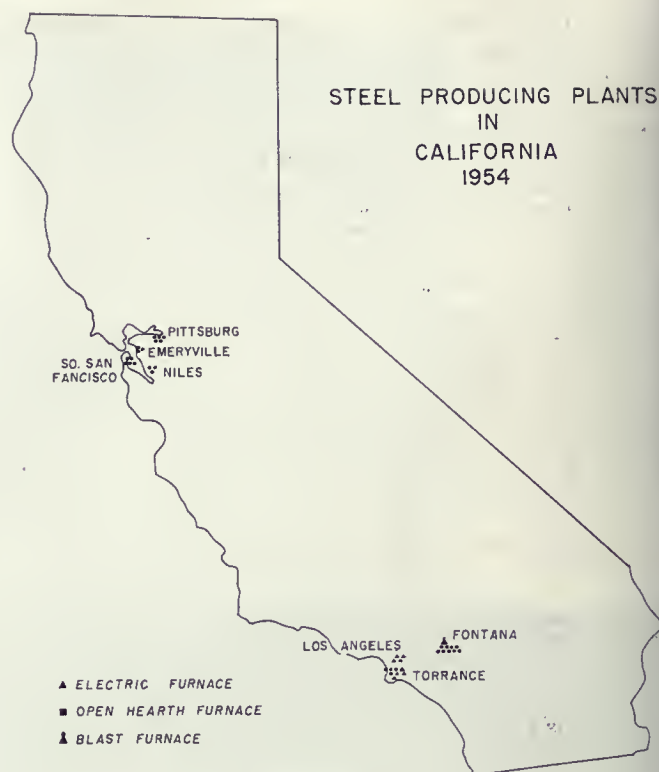


FIGURE 12.

aggregate, ship ballast, paint pigment, or heavy media, or as an ingredient in ferroalloys, foundry sand, or drilling mud.

Because it is a commodity of relatively low unit value, and must be produced in large volumes, iron ore is mined as inexpensively as possible, ordinarily by open pit methods. At the Eagle Mountain mine of Kaiser Steel Corporation (Huseman, 1953 and 1955), for example, ore is churn-drilled and blasted in 30-foot benches, then loaded by electric and diesel shovels into trucks which haul it to be crushed, beneficiated as necessary, and stock-piled. These large-scale efficient methods enable this ore to be mined, hauled, crushed, and loaded aboard railroad cars for a total cost of about 50 cents per net ton in 1953 (Powell 1953, p. 8). All of the other productive iron mines in California have also been mined by open-pit methods, although necessarily on a smaller scale, and at somewhat higher cost per ton.

Economical transportation methods are also required for successful marketing of iron ore. The length of truck roads or railroad that must be built to develop a new deposit, and the distance the ore must be hauled to market are important factors to the shipper. Kaiser Steel, for example, constructed 51 miles of standard gauge track from Ferrum Siding on the Southern Pacific Railroad to Eagle Mountain mine, to enable ore to move by rail the 163 miles to Fontana.

Haulage, both of raw materials and of finished steel products, is of prime importance in the competition between steel producers for California markets. Total ton miles to assemble the raw materials for one ton of pig iron at Fontana is 1,522 (iron ore 309; coal 1,212; and flux 1) compared to figures of 635 at Provo, Utah; 49 at Birmingham, Alabama, and 604 at Pittsburgh, Pennsyl-



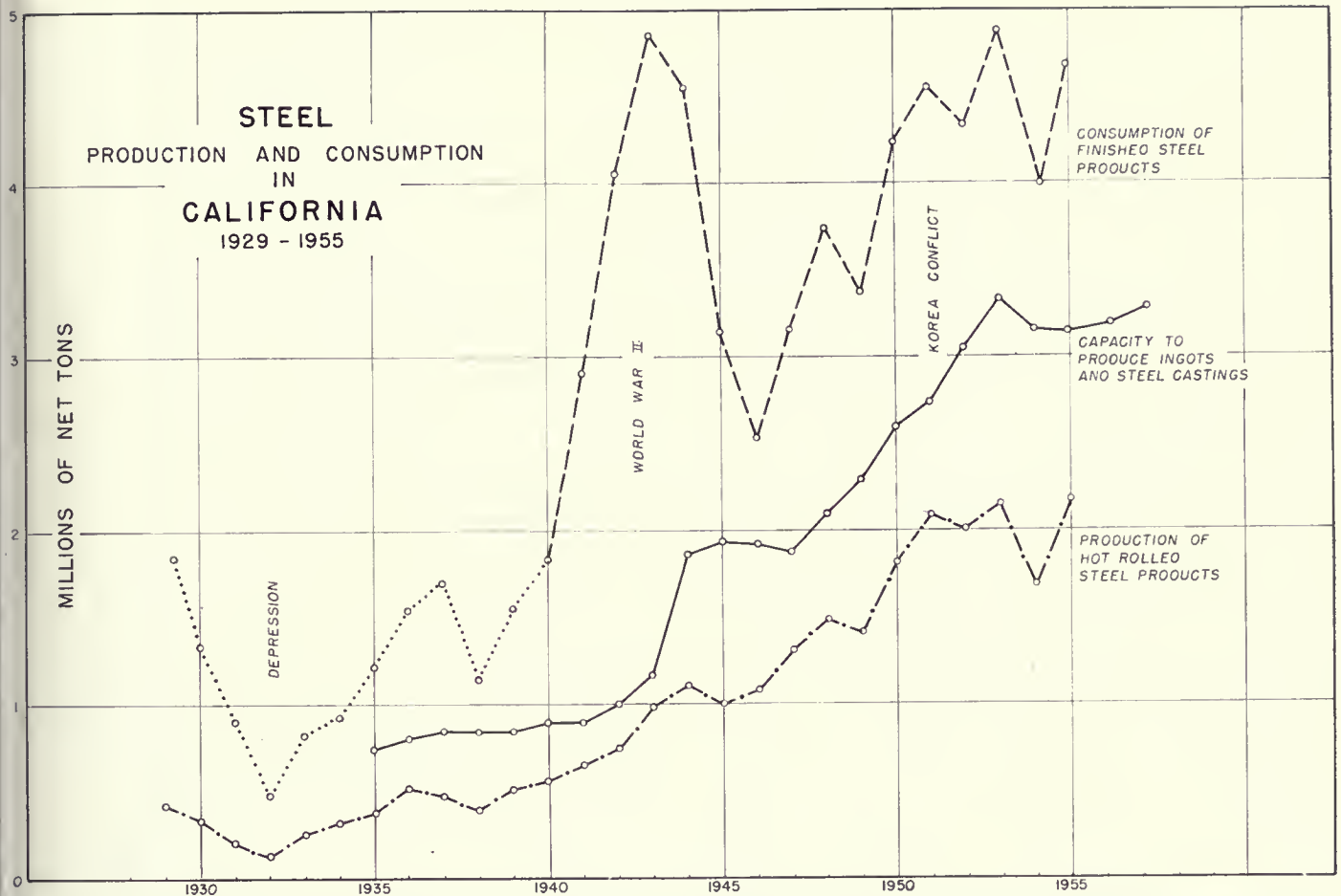


FIGURE 13. Data from estimates prepared by General Planning Department, Kaiser Steel Corporation, and Commercial Research Department, Columbia-Geneva Steel Division, United States Steel Corporation and from American Iron and Steel Institute. Pre-1940 consumption estimated at 70 percent of total for seven western states (California, Oregon, Washington, Idaho, Utah, Nevada, Arizona) in U. S. Bur. Mines Minerals Yearbooks.

vania (Grether 1946, p. 76). Once assembled, however, the shorter haulage of finished steel from Fontana to west coast markets makes up much of the difference. The total ton miles of haulage required to assemble raw materials for one ton of steel, and to deliver the finished steel to consumers in Los Angeles, is 1,580 for the Fontana plant, compared with 1,382 for Provo, 2,165 for Birmingham, and 3,228 for Pittsburgh (Grether, 1946, p. 76). Corresponding total haulage for delivery of a ton of finished steel for consumption in San Francisco are 2,048 from Fontana, 1,495 from Provo, 2,663 from Birmingham, and 3,332 from Pittsburgh. Although it would appear that haulage costs for delivery of finished steel to California markets should be less from Fontana than from Provo, the unusually long haul of coal to Fontana gives a small overall advantage in transportation costs to the Utah steel. The haulage advantage of both of these western steel-producing centers over their eastern competitors, although notable, is insufficient to prevent competition in many classes of steel products.

#### STEEL

Steel is a commercial form of iron which contains a maximum of 1.7 percent carbon as an essential alloying constituent. When iron is drawn from the blast furnace

as hot metal or pig iron, it contains about 3.5 to 4.5 percent of carbon, which is absorbed from coke in the blast furnace. About 1.7 percent of the carbon is in solution in the iron, and gives rise to few or no adverse properties. The carbon in excess of 1.7 percent is disseminated as graphite flakes and as iron carbide, which tends to make the pig iron hard and brittle. The primary function of the steel-making process is to reduce the carbon content below the critical 1.7 percent level.

For many purposes steel is more useful than iron because of its greater strength, hardness, malleability when cast, and resilience. A wide variety of useful properties may be imparted to special or alloy steels by additions of appropriate alloying elements, the most common of which are manganese, chromium, nickel, molybdenum, tungsten, vanadium, silicon and copper. The special properties imparted to steel by these alloying constituents include hardness, stiffness, ductility, resilience, tensile strength, compressive strength, resistance to fatigue, resistance to abrasion, resistance to corrosion, and ability to hold a cutting edge at high temperature.

Prior to 1942, when Kaiser Steel Corporation commenced to produce iron at Fontana, all of the steel used in California was brought into the state, either in fin-



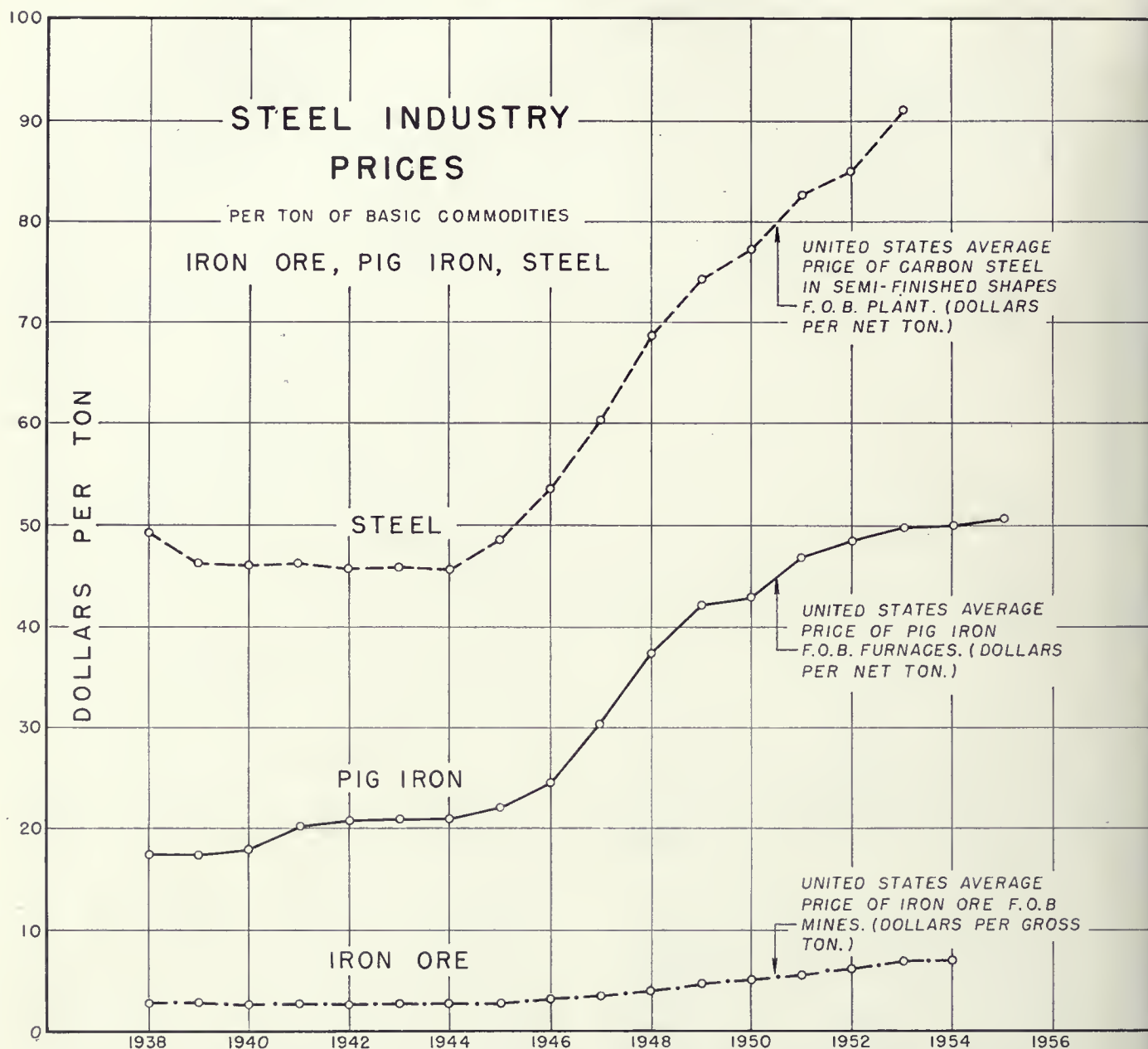


FIGURE 14. United States average prices for iron ore, pig iron, and semi-finished carbon steel, showing the relationships between costs of these basic commodities of the steel industry, 1938 to 1955. Finished grades of certain types of steel commonly cost five to ten times as much as the prices shown for carbon steel. Data from U. S. Bur. Mines Minerals Yearbooks and Mineral Market Reports.

ished form or in the form of pig iron or scrap metal to be converted into steel. Before World War II, the steel industry in California consisted essentially of small- or moderate-sized rolling mills, with furnace capacity for melting scrap. They depended mainly on local supplies of scrap metal, and were equipped to roll a limited variety of products.

During the several decades prior to 1940, most of the steel plants in California gradually were merged into two larger companies, Pacific Coast Steel Company and Columbia Steel Company, but both were still small compared to most steel plants in the eastern United States. In 1929-30, Pacific Coast Steel Company was absorbed by Bethlehem Steel Company, and became known as

Bethlehem Pacific Coast Steel Corporation; and Columbia Steel Company became a subsidiary of United States Steel Corporation, and the production division became known as Columbia-Geneva Steel Division, United States Steel Corporation.

During World War II, an acute demand developed for steel for use in the defense plants of the West Coast. Two new plants were built in California; one by Pacific States Steel Company at Niles, Alameda County, and the other by Kaiser Steel Corporation at Fontana. After the war demand for steel on the Pacific Coast in California continued to increase, leading to further expansions of steel-producing capacity, and diversification of steel products manufactured to meet peacetime demands.



# FLOW CHART OF STEEL MAKING

RAW MATERIALS	IRON	STEEL
<p><b>IRON ORE</b></p> <p>Typical oxide ore:</p> <p>Fe 53% P 0.1% SiO<sub>2</sub> 10% Al<sub>2</sub>O<sub>3</sub> 2% CaO 3% MgO 5% S 0.5% Mn 2%</p> <p>Size 7 - 1 in.; fines are sintered</p> <p><b>COKE</b></p> <p>Coke is produced by heating bituminous coal for 17-20 hours at 2000-2140° F in a sealed oven in absence of air. Typical coke contains carbon 85-93%, ash 7-15%, sulfur 0.5-1.25%, residual volatiles 0.5-3%, should be strong, in large lumps. 1 ton coal yields about 70% coke, 11,000 cu. ft. gas (550 B.t.u. per cu. ft.), 9 gal. tar, 3 gal. light oil, 23 lbs. ammonia</p> <p><b>LIMESTONE</b></p> <p>Limestone: Desired as pure CaCO<sub>3</sub>, free from silica, clay, sulfur, etc. Magnesian limestone (dolomite) is sometimes used. Lumps desired, 1-8 in.</p>	<p><b>BLAST FURNACE</b></p> <p>Input: 1 ton of hot metal requires about 1 3/4 ton ore, 3/4 ton coke, 1/2 ton limestone, and 3 1/2 tons of preheated air blast</p> <p>Output: Slag removes much impurity, but all phosphorus, much silicon, manganese, sulfur remain in molten iron ("hot metal") which also absorbs carbon. Blast furnace exhaust gases furnish heat for other processes</p> <p>Typical analysis of hot metal (No. 2 Foundry pig)</p> <p>Fe 91-93 1/2 % P 0.5-1.0 % S 0.045 % max. Mn 1.0% max. Si 2.0-2.5% C 3.0-4.5%</p> <p>Molten metallic iron produced by reduction of iron oxide in ore by action of coke burning in hot air blast</p> <p>Impurities mostly combine with limestone flux, are removed as slag</p>	<p><b>OPEN HEARTH PROCESS</b></p> <p>Burning air-gas mixture melts charge, impurities removed in slag</p> <p>Input: Pig iron (molten or cold) about 30-50%, scrap 40-60%, limestone 5-10%, iron ore 3-5%, fluorspar flux, re-carburizers, and ferroalloys as needed for desired steel</p> <p>Output: Refined steel about 90%, slag 10%</p> <p>Time: 8-12 hrs; 2800-3100° F</p> <p><b>ELECTRIC FURNACE PROCESS</b></p> <p>used to produce high-quality and special alloy steels</p> <p>Heat of electric arc melts cold charge (80-100% scrap) oxidizes impurities as slag.</p> <p>Special ingredients and ferroalloys added to produce desired steel</p> <p>Time: 4-12 hrs; 3500° F or more (Produced about 7% of U.S. steel in 1955)</p> <p><b>BESSEMER PROCESS</b> (not in use in California)</p> <p>Impurities removed from molten metal by oxidizing effect of compressed air forced through jets in bottom of converter.</p> <p>Air blast lasts 12-15 minutes, removes nearly all Si, Mn, C at 2700-2900° F. Exact amounts of Si, Mn, C, and ferroalloys added to produce desired steel</p> <p>(Produced about 5% of U.S. steel in 1955)</p>

FIGURE 15.



During the period 1950-56, the principal demand for steel products in California has been for sheared plate, sheets and strip, tin plate, and pipe products. The local demand for heavy plate, structural shapes and bars used in heavy fabrication and construction industries has increased at a much slower rate.

In southern California, where more than 50 percent of the state's steel market exists, the principal demand is for sheet and strip to supply the many small metal-working plants, and for pipe to supply the construction and oil industries. In northern California the principal demand is for tin plate for use by the food canning industry, and for plate to be used in the manufacture of large-diameter pipe, such as is used for gas transmission lines.

By industries, consumption of steel in California is similar to the rest of the west, where about 35 percent of the steel consumed goes into the construction industry; about 40 percent into the railroad, oil and gas, and container industries, and about 25 percent into the automotive and all other industries (Cort, 1955, p. 33). Rails and oil country goods, such as drill pipe, are the main types of steel products not made in California.

*Steel Manufacture.* Steel-making involves the melting of pig iron or scrap iron, or a mixture of the two; the removal of detrimental substances (such as excess carbon, silicon, phosphorus, and sulfur); and the addition of desirable substances in the form of ferroalloys to produce steel of the desired characteristics. The two steel-making methods common in California utilize the basic open-hearth furnace, in which about 80 percent of this state's steel is manufactured, and the electric furnace. Kaiser Steel Corporation has announced that the first facilities in the west for making steel by the basic oxygen furnace process will be in operation at the Fontana plant by early 1958. Open-hearth furnaces, which have larger capacities than electric furnaces, are used to make most commercial or carbon steel which contains no essential alloying constituents other than carbon. Electric furnaces, which cost less to build than open-hearth furnaces and allow closer control of steel composition, are used to make nearly all special alloy steels, as well as an increasing percentage of carbon steel.

The charge for open-hearth furnaces ordinarily consists of limestone, steel, scrap, and pig-iron (molten or cold). When hot metal constitutes more than 55 percent of the charge, iron ore is added to the cold charge; about 10 to 12 percent of the open-hearth charge at the Fontana plant is iron ore. Coke-oven gas and natural gas are the principal fuels used in the open-hearth furnaces in California. During the melting process, fluorspar is added to thin the slag and improve its capacity to absorb undesirable impurities. In the later stages of the process, several percent of iron oxide in the form of iron ore or roll-scale, may be added as a source of oxygen to control carbon content; ferroalloys may be added just before or during tapping. Impurities are removed in the lime-silicate slag and the finished steel poured into ingot molds to harden for milling to usable shapes.

Electric furnaces, in which heating may be accomplished either by electric arcs or induction, are charged



FIGURE 16. Tapping finished steel from open hearth furnace at Fontana plant of Kaiser Steel Corporation. Larger receptacle (center) is the teeming ladle, which will be carried by an overhead crane so the steel may be poured into ingot molds to harden. Smaller receptacle (right) is the slag ladle, which receives the impurity-laden slag for disposal or reuse. Barely visible behind the ladles is the external brickwork of the checker stoves beneath the furnace, in which the gases that fire the furnace are preheated. Photo courtesy of Kaiser Steel Corporation.

with about the same ingredients as open-hearth furnaces, and the steel-making process is very similar. Ore, cinder, roll-scale, and lance-injected oxygen are used to lower the carbon content. Limestone, lime, silica sand, crushed coke, aluminum, and fluorspar are added as slag constituents. The nature of the steel made in a given heat is controlled by such factors as the composition of the raw materials charged, the composition of the slag, the temperature of the melt, and the amount and nature of deoxidizing, decarbonizing, or alloying constituents added. All general classifications of steel, which include carbon, alloy, stainless and heat resisting, and tool and die, are made in electric furnaces.

Scrap metal and metallic iron (hot metal and pig iron) can be used interchangeably in various proportions in the charge for both open-hearth and electric steel furnaces, depending mainly on their relative availability and cost. The Kaiser Steel Corporation Fontana plant, the only hot-metal plant in California, uses 60 to 70 percent hot metal with 40 to 30 percent scrap for open-hearth charge. Cold-metal plants in California, which include both electric and open-hearth operations, commonly use 80 to 90 percent of scrap metal. At the



Table 5. List of some common ferro-alloys with approximate range of composition of major constituents by percent, omitting minor percentages of sulfur and phosphorus. (Data compiled from Bray, 1942, p. 425; and Herzog, 1948).

Material	Principal constituents (percent)												
	Fe	C	Si	Mn	Cr	Al	Ca	V	W	Ti	Mo	Zr	Cb
Ferromanganese (standard).....	10-14	6.75	1	78-82									
(medium C).....	11-17	1.5	1.5-2.5	80-85									
Spiegeleisen.....	75-90	4-5	1	5-20									
Silicospiegel.....	58-68	2-4	5-8	25-30									
Silicomanganese.....	7-20	1-3	14-20	65-70									
Ferromanganese-silicon.....	25-30	0.6	47-54	20-25									
Ferrosilicon 15%.....	74-84	1	14-20										
50%.....	51-47		43-52										
85%.....	10-16		82-88										
Ferrochromium (low C).....	26-32	0.6-2.0			67-72								
(high C).....	23-29	4.5-7.0			66-70								
Calcium-aluminum-silicon.....			50-53			8-12	10-14						
Ferrovandium.....	49-63	3-0.2	8-1.5					35-40					
Ferrotungsten.....	16-22	.25-2.0							78-82				
Ferrotitanium.....	33-73		3-13			2-9				20-45			
Ferromolybdenum.....	22-43	2.5									55.75		
Ferrozirconium.....	8-12	0.5	47-52									35-40	
Ferrocolumbium.....	33-43	0.5	7										50-60

close of 1956, scrap steel (number 1 heavy melting) cost \$55 per gross ton delivered in San Francisco, and \$54 per ton in Los Angeles, whereas basic pig iron cost \$70 per gross ton f.o.b. Fontana, and \$62.50 at Geneva, Utah. The rail haulage rate from Geneva to San Francisco was \$9.39 per ton.

#### FERROALLOYS

Ferroalloys are artificially prepared iron-bearing alloys so rich in some element other than carbon that they may be used as a vehicle for introducing that element in the manufacture of iron or steel. Some products that contain little or no iron are also commonly listed as ferroalloys (table 5).

Ferroalloys are used principally in the steel-making industry where they serve several functions (table 6). Some are intended to remain in the steel to give it special physical properties which are determined by the type and proportions of the alloying materials used. Ferroalloys that are used principally for this purpose include ferromanganese, ferrosilicon, ferrochromium, ferrotungsten, ferromolybdenum, ferrovandium, and to a lesser extent, ferrotitanium, ferrouanium, ferrophosphorus, silicon-zirconium, and other less common materials.

A more widespread use for ferroalloys is as deoxidizing or cleansing agents, which are used in the making of all types of steel. The ferroalloy metals used principally for this purpose are manganese (as ferromanganese) and silicon (as ferrosilicon); aluminum, calcium and vanadium are also effective deoxidizing agents. In this usage, the ferroalloys are added during the final stages of steel preparation. They combine with oxygen, sulfur, or other unwanted substances in the melt, and the reaction products join the slag for removal.

Another usage of ferroalloys is to neutralize the undesirable effects of certain substances by combining with them in a harmless form that remains in the finished steel. The combination of manganese with sulfur to form harmless sulfides is an example. Another function of certain ferroalloys is the removal of gas from the molten metal so that bubbles ("blowholes") do not form in the ingots. Several of the ferroalloys perform two or

more of these types of functions according to the amount added, and the stage in the processing of the melt when they are added.

Table 6. List of commonly used ferroalloy materials with the properties they impart to molten and finished steel. (Data adapted from Stoughton, 1934, pp. 490-530; Bray, 1942, pp. 424-433; Geehan, 1956, p. 277.)

Substance	Percent used	Principal effect in steel
Aluminum*.....	0.03-0.1	Deoxidizes; degases; increases surface hardness.
Boron.....	0.001-0.01	Increases hardenability.
Calcium*.....		Deoxidizes; degases; increases fluidity.
Chromium.....	1-5	Increases hardness and depth hardening.
Chromium.....	11.5-38	Eliminates corrosion (stainless steels); reduces scaling.
Cobalt.....		Imparts high-temperature stability; resistance to corrosion, and useful magnetic properties; (with nickel) minimizes coefficient of expansion.
Columbium.....		Inhibits intergranular corrosion in stainless steel; mainly used in high-temperature steels.
Copper.....	0.15-0.50	Reduces corrosion.
Manganese*.....	up to 1.5	Deoxidizes; neutralizes effect of sulfur.
Manganese.....	1-2	Increases strength and toughness.
Manganese.....	7-14	Imparts properties of progressive work-hardening and resistance to abrasion.
Molybdenum.....	0.25-0.75	Increases elasticity (hence workability), tensile strength, hardenability and resistance to shock; imparts high-temperature strength.
Nickel.....	1.50-4.50	Decreases corrosion at high temperatures; reduces fatigue; increases hardness (e.g. armor plate), tensile strength, and toughness; imparts useful magnetic qualities; (with cobalt) minimizes coefficient of expansion.
Phosphorus.....		Usually detrimental (causes brittleness and low resistance to impact) but used in special cases to improve machinability and electrical properties; increases fluidity of cast iron.
Selenium.....		Improves machinability, especially in stainless steels.
Silicon.....	0.1-0.2	Deoxidizes; reduces incidence of "blowholes" in ingots; increases tensile strength.
Silicon.....	2-4.75	Improves efficiency in electromagnet cores.
Silicon.....	13	Increases resistance to acid attack.
Sulfur.....		Usually detrimental; used in special cases to improve machinability.
Titanium.....		Inhibits grain growth and intergranular corrosion in stainless steels; deoxidizes; desulfurizes; degases (nitrogen).
Tungsten.....	14-18	Imparts hardness and strength at high temperatures ("red hardness") in tool steels.
Vanadium.....	0.15	Refines grain size; imparts high-temperature strength and hardness; increases ductility and resiliency.
Zirconium.....		Deoxidizes; desulfurizes; fixes nitrogen.

\* May also be added as native metal or oxide.





FIGURE 17. Tapping approximately 80 tons of finished steel from one of the three electric-arc furnaces at the Los Angeles plant of Bethlehem Pacific Coast Steel Corporation. (Photo courtesy of Bethlehem Pacific Coast Steel Corporation.)

Ferroalloys generally are added to the molten steel in lumps or briquets, ranging in size from one inch to 75 pounds, but in some practices they are added in the molten state, or as shot. In electric furnace practice, the ferroalloys and other alloy materials that are not easily oxidized are usually charged into the furnace before melting down. Most of the ferroalloys used to adjust the composition of the steel to meet specifications are added in the late stages of the process before tapping, or to the ladle during tapping.

The iron foundry industry provides another market for ferroalloys, mainly the variety of ferrosilicon that contains 5 to 20 percent silicon and is known as silvery pig iron. Of the 873,000 short tons of ferrosilicon, silicon metal, and miscellaneous silicon alloys consumed in the United States in 1953, nearly half was consumed by iron foundries and miscellaneous users (Geehan, 1957, p. 457). The miscellaneous users included firms that consumed silicon metal in the production of aluminum and magnesium products, and the manufacture of low carbon and non-ferrous alloys. From 1942 to 1944, and 1951 to 1953, the Kaiser Magnesium Company plant at Manteca, San Joaquin County, consumed ferrosilicon containing 75 percent silicon in the production of metallic magnesium by the Pidgeon process. A small tonnage of ferrosilicon is also ground for use in the heavy media separation process for ore beneficiation.

*Manufacture of Ferroalloys.* In 1953, ferroalloys were made in 12 blast furnace plants, 39 electric furnace plants, and four aluminothermic plants in the United States. In that year, 2,336,286 short tons of ferroalloys were produced in the country. Of this total, about 39 percent was ferromanganese, about 35 percent ferrosilicon, about 12.2 percent ferrochromium and other chromium ferroalloys, about 9.7 percent spiegeleisen, silicomanganese, and manganese briquets, 2.3 percent ferrophosphorus, 0.5 percent ferrotitanium and ferrovanadium combined, 1.0 percent ferrotungsten, ferromolybdenum, and other molybdenum products, and about 0.8 percent all other ferroalloys combined (Geehan, 1957, p. 453). All ferroalloys except high-carbon ferromanganese, some low-manganese alloys such as spiegeleisen, and low-silicon ferrosilicon, are made in electric furnaces because their greater heat is required to reduce some of the refractory oxides of the alloy metals, and to produce low-carbon alloys.

Materials placed in the furnaces to produce ferroalloys generally include low sulfur, low phosphorus, iron in the form of soft iron or steel scrap or turnings; a carbonaceous reducing agent such as charcoal or high-grade coke low in phosphorus and sulfur; silicon as quartzite; high grade ores of the alloy metal; and slag-forming materials as necessary (Mantell, 1940, pp. 490-501).

Ferroalloys, including ferromanganese, silico-manganese, and ferrochromium, were first produced in California during World War I at Heroult, Shasta County, by the Noble Electric Steel Company (Bradley, et al., 1918, pp. 20-22) which utilized Shasta County iron ore, and manganese and chromium ores from other parts of the state. Two electric furnaces, each with capacity of 7 to 8 tons every 24 hours, were used to produce ferromanganese that ranged from 70 to 80 percent manganese, 20 to 12 percent iron, 6 percent carbon, 1 to 3 percent silicon, and a trace of phosphorus and sulfur. To make the 80 percent product, the furnace was charged with one ton of ore containing 50 percent manganese, about 16 percent silica, 1 to 3 percent iron, and no more than traces of sulfur and phosphorus; 800 pounds of limestone; 60 pounds of fluorspar; 70 pounds of iron ore; and 550 pounds of crushed charcoal or coke. Local petroleum coke was used when available at competitive prices.

A smaller electric furnace was used intermittently to produce ferrosilicon of 75 percent silicon content. The furnace charge for this product was one ton of siliceous material with 85 percent silica and 5 to 10 percent iron; 1000 pounds of charcoal; and 400 pounds of iron ore containing 68 percent iron and 1 to 2 percent silica.

Also during World War I the Pacific Electro Metals Company (later the Pacific Alloy and Steel Company) made ferromanganese and silico-manganese at Bay Point, Contra Costa County (Huguenin and Castello, 1921, pp. 66-67). Manganese ore, containing a minimum of 40 percent manganese and not more than 18 percent silica, was charged with coke and iron turnings up to 3 inches diameter in two electric furnaces of 12 tons per day capacity. Some of the coke was petroleum coke from local refineries. The silico-manganese produced contained 50 to 55 percent manganese, 20 to 25 percent silica, and maxima of 1 percent carbon, 0.18 percent phosphorus, and a trace of sulfur.





FIGURE 18. Hot rolling a steel shape in the 3-stand 29-inch structural mill of Kaiser Steel Corporation's Fontana plant. The two 2-high roll stands at left, and the single 1-high stand (center) are operated from the air-conditioned pulpits suspended above. (Photo courtesy of Kaiser Steel Corporation.)

The most recent and largest production of ferroalloys in California was by the Permanente Metals Corporation (later Kaiser Aluminum and Chemical Corporation) at Permanente, Santa Clara County. The plant was active from August 1942 through August 1947, in April, May, and December 1949, and from February 1951 through June 1953. Two grades of ferrosilicon, containing 50 percent and 75 percent silicon, were made in the plant's three 8000 KVA electric furnaces. Each furnace had a capacity of 1000 tons of 50 percent grade per month, or 575 tons of 75 percent grade. The furnace charge consisted of steel turnings, quartz, petroleum coke, metallurgical coke from Alabama, and coking coal from Kentucky. Specifications for the quartz required at least 98 percent silica ( $\text{SiO}_2$ ), and a size range between  $\frac{1}{2}$  and  $3\frac{1}{2}$  inches. Crushed vein quartz was obtained from the White Rock mine, Mariposa County, and from hand-

sorted quartz cobbles from Bear River, Nevada and Placer Counties.

From 1942 to 1944, and from June 1951 to June 1953, the 75 percent grade was made, for making magnesium at the government owned plant at Manteca operated by the Kaiser Magnesium Company. Most of the production from 1945 to 1950 was the 50 percent grade, largely consumed in steel-making by the Kaiser Steel Corporation at Fontana. The closing of the magnesium plant at Manteca, together with unfavorable market conditions for the sale of ferrosilicon, contributed to the final cessation of ferroalloy production at the Permanente plant in 1953. The Permanente plant has been operated periodically since 1953 to produce volatilized amorphous silica, in particles three to four microns in size, to be used as a binder in making periclase refractories in the Company's refractory brick plant at Moss Landing, Monterey County.



Table 7. *Prices of some common ferroalloys, as of January 2, 1957, from E. & M. J. Metal and Mineral Markets, January 10, 1957, p. 8. Prices recalculated from "per pound of contained metal" to "per pound of ferroalloy" basis for purposes of comparison.*

Material	Specifications	Price	
		Per pound of ferroalloys	Per ton of ferroalloya
Ferromanganese----- 74-76% Mn	Standard grade, C/L lots, lump, bulk, f.o.b. plant.	\$0.1175-.1275	\$235-\$255
Ferromanganese----- 90% (max. 0.07% C)	Low-carbon grade, C/L lots, lump bulk, f.o.b. plant.	\$0.3037-.3159	\$607-\$632
Ferrosilicon----- 50% Si	C/L lots, bulk delivered.	\$0.0695	\$139
Ferrosilicon----- 75% Si	C/L lots, bulk, delivered.	\$0.1260	\$252
Ferrochromium----- 65% Cr (4-9% C)	High-carbon grade, C/L lots, bulk delivered.	\$0.1802	\$360
Ferrochromium----- 65% Cr (max. 0.5% C)	Low-carbon grade, C/L lots, bulk, delivered	\$0.2486	\$497
Ferrotungsten----- 80% W	Lots of 5,000 lbs. or more, ¼-in. lump, delivered	\$2.52	\$5,040
Ferromolybdenum----- 60% Mo	Lots of 5,000 lbs. or more, powder, f.o.b. plant.	\$1.044	\$2,088
Ferrotitanium----- 40% Ti (max. 0.10% C)	Low-carbon grade, lots of ton or more, ½-in. lump, f.o.b. plant.	\$0.540	\$1,080
Ferrovanadium----- 50% V	Crucible grade, C/L lots, packed, f.o.b. plant.	\$1.70	\$3,400
Ferrocolumbium----- 60% Cb. (max. 0.40% C, max. 8% Si)	Ton lots, packed, 2-in. lump, f.o.b. destination.	\$4.14	\$8,280

Almost all of the ferroalloys consumed in California are used in the making of steel. Carbon steels, which comprise an estimated 95 percent of this state's steel production, require an average of about 25 to 30 pounds of ferroalloy per ton of steel—almost entirely divided between ferromanganese and ferrosilicon in near equal proportions. An estimated total of 40 to 50 thousand tons of these two ferroalloys was consumed in California in 1956. The remaining 5 percent of steel made in California is of special grades with ferroalloy content ranging from two to more than 50 percent. In 1956, an estimated 10 to 15 thousand tons of ferroalloys were consumed in special steels made in California. This consumption involved mainly ferromanganese, ferrochromium, and ferromolybdenum, but included smaller amounts of many other ferroalloys.

Most of the ferroalloys consumed in California are brought by rail from Oregon, Utah, and many eastern states. Prices of representative ferroalloys are listed in table 7; for delivered prices in California, add \$10 to \$25 per ton to f. o. b. plant prices.

### COKE

Metallurgical-grade coke has been produced in California only since the establishment in 1943 of the Kaiser Steel Corporation coke plant at Fontana. California has yielded but small amounts of coal and none of coking grade (see section on coal in this volume). Coke is produced at the Fontana plant from coal shipped mainly from deposits in Utah, Oklahoma, and Arkansas. Between 100,000 and 200,000 tons of prepared coke have been brought into the state each year since 1950 for use in foundries and other industrial plants.

Coke is the residue that remains after certain bituminous coals have been subjected to a prolonged heating out of contact with air. The nature of the coal, as well as the time and temperature in the coke oven, determine the quality of the coke. Bituminous coals that are low in ash, sulfur, and phosphorus yield the best coke. Common metallurgical grades of coke include blast furnace coke, used in iron blast furnaces; and foundry coke, which is used mainly in iron and steel foundries.

Blast furnace coke should be in large lumps (usually 60 to 70 percent larger than 2 inches) that are hard and strong enough to resist breakage during handling, and when in the furnace. It should be porous enough to permit efficient combustion without excessive solution waste. It should produce a minimum of smoke or volatile products, and should neither fuse nor cake when used. It should contain a high proportion of fixed carbon (85 to 90 percent is desired) and a minimum of sulfur (0.6-1.5 percent) and phosphorus (less than 0.04 percent). Volatile matter should be less than 2 percent, moisture not more than 3 percent, and ash not more than 10 percent (Bray 1942, pp. 60-61). Foundry coke is cooked longer, forms firmer and larger lumps, and may be made from different coals than blast furnace coke.

The suitability of coal for the production of coke can not be determined by chemical analysis alone, but must be ascertained by actual tests in a coking oven. The California coals that have been thus tested have proved to have a high ash content that weakens the resulting coke.

In the United States, coke is produced in both beehive and byproduct ovens. More than 90 percent of the nation's output is obtained from the byproduct process, which is preferred because (1) it yields at least 15 percent more coke per ton of coal than the beehive process, (2) volatile byproducts of considerable value are recovered, and (3) many coals not suited to the beehive process may be used in byproduct ovens when blended with other coals (Hudson 1942, p. 34).

Coking facilities at the Fontana steel plant have been increased from 90 ovens (capacity 355,000 tons of coke per year) in 1943, to 225 ovens (capacity of 1,055,000 tons of coke per year) in 1953. All are Koppers-Becker slot type byproduct ovens, 40 feet long, 13 feet high, and about 14 inches wide inside. About 25 tons of coal, crushed so that 50 percent passes a ½ inch screen, are charged into the oven, filling it nearly to the top. The oven is then sealed shut and heated by blast furnace gas to about 950°C for 16 to 17 hours. As the volatiles are expelled they are piped to an adjacent byproduct plant where ammonium sulfate, tar, creosote oil, distillate, phenol, fuel oil, benzol, toluol, xylol, naphtha and other light oil products are recovered. When ready, the coke is pushed out of the oven, quenched with water and screened.

In 1955, the Fontana plant \* consumed 1,356,513 short tons of coal and yielded 805,566 tons of blast furnace coke for use in the company's blast furnaces; 2,798 tons of coke for other industrial purposes; and 67,142 tons of breeze (fragments smaller than ½ inch). About 83 percent (1,136,782 tons) of the coal consumed was high-volatile coal (containing more than 31 percent dry volatiles) with which low-volatile coal (containing 14 to 22

\* Statistical data in this section from Sheridan, et al., 1956, and DeCarlo and Otero, 1956.



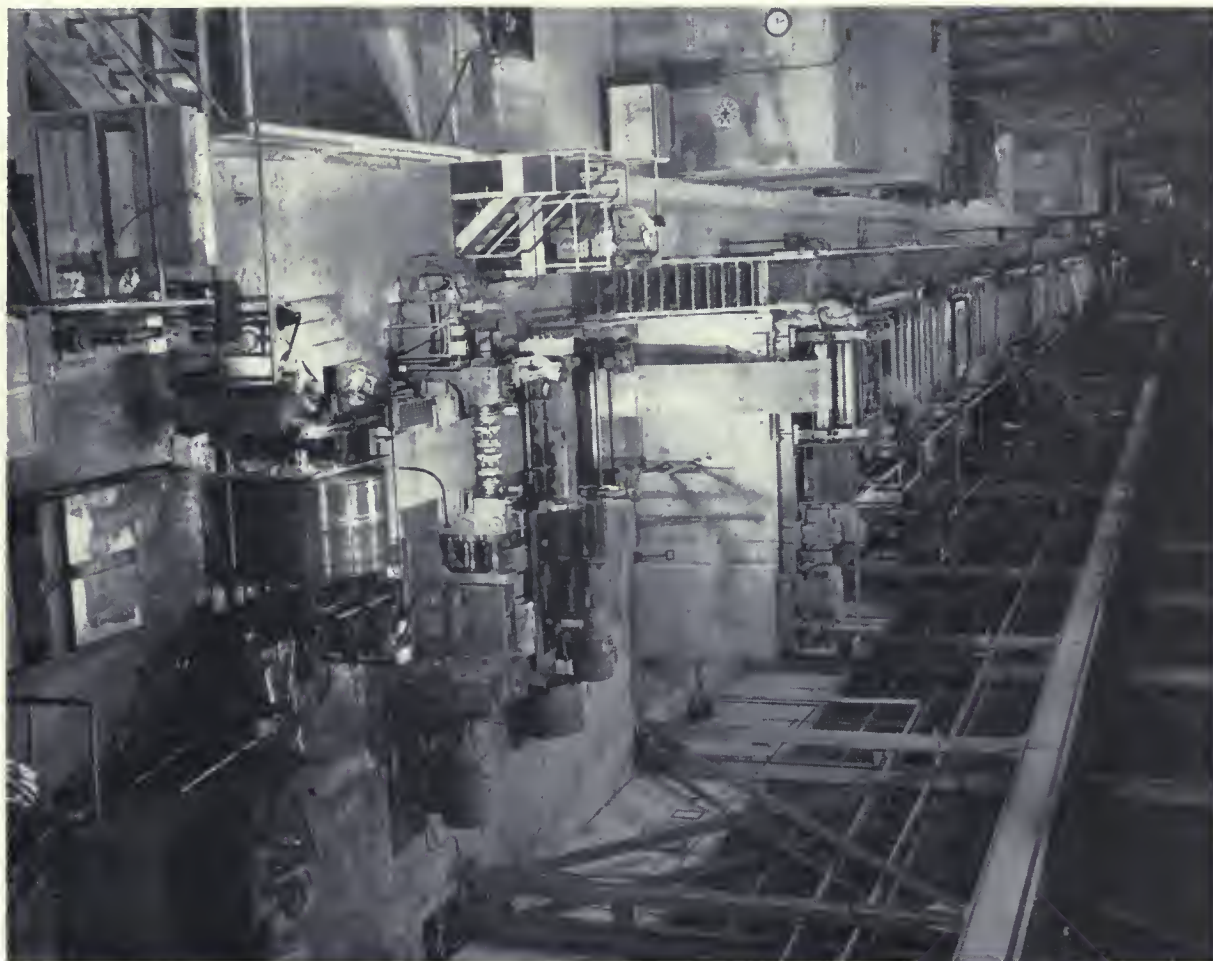


FIGURE 19. Pickling steel strip (preparing its surface), preliminary to coating it with tin, at the tin plate mill of Kaiser Steel Corporation's Fontana plant. Both hot dip and electrolytic tinning processes are used to produce tin plate, primarily for consumption as tin cans by California's food canning industry. (Photo courtesy of Kaiser Steel Corporation.)

percent dry volatiles) was blended before charging, in order to make stronger coke. In 1955, most of the high-volatile coal (1,121,743 tons) was obtained from the company-owned Sunnyside mine in Utah; and low-volatile coal came mainly from Oklahoma (223,591 tons). New Mexico supplied 12,366 tons, Arkansas sup-

Table 8. Average yield per ton of coal carbonized at Fontana in 1955, and average value for such materials recovered in the United States in 1954. (Fram DeCarlo and Otero, 1956).

Product	Amount	Value
Coke.....	1,201 pounds	\$11.439
Breeze.....	99 pounds	0.237
Coke-oven gas.....	11,480 cubic feet	1.489
Coke-oven tar.....	9.13 gallons	1.003
Coke-oven ammonia..... (sulfate equivalent)	23.87 pounds	0.352
Crude light oil.....	3.34 gallons	0.839
Benzene (all grades).....	1.84 gallons*	
Toluene (all grades).....	.53 gallons*	
Xylene (all grades).....	.13 gallons*	
Solvent naphtha (crude and refined).....	.09 gallons*	
Others.....		0.021
	Total.....	\$15.380

\* Derived from the 3.34 gallons of crude light oil also listed.

plied 9,174 tons, and Colorado supplied 2,673 tons of coal of undetermined types.

The 808,364 tons of coke produced in California in 1955, although vital to this state's iron industry, amounted to only 1.06 percent of the total United States production for that year. With the exception of 35 tons shipped to Arizona in 1955, the entire output of blast furnace coke at the Kaiser Fontana plant has been consumed in the company's blast furnaces nearby.

About 45,000 tons of breeze have been used at the Kaiser steel plant each year since 1950. It is ground so that 50 percent passes a  $\frac{1}{8}$  inch sieve, and used principally as fuel in the sinter plant, and to line floors of soaking pits, in the steel plant. Relatively minor tonnages of breeze have been exported, or shipped to other western states. The total tonnage shipped out of California each year has increased steadily from about 700 tons in 1952 to more than 12,000 tons in 1955.

In 1955 some 1,200 pounds of coke per ton of coal was obtained at Fontana, whereas the national average was 1,400 pounds. Of the coke consumed in California in 1955, about 85 percent (805,566 net tons) was used in the Kaiser Steel Corporation blast furnaces; foundries accounted for about 7 percent (78,016 tons); and





FIGURE 20. Rolling a 9,000 pound steel ingot at 2300° F. in a 32-inch rolling mill at the Los Angeles plant of Bethlehem Pacific Coast Steel Corporation. Rolling reduces the cross section of the ingot to billet size, and improves the internal structure of the steel. (Photo courtesy of Bethlehem Pacific Coast Steel Corporation.)

other industrial plants consumed about 8 percent (66,632 tons). In 1954, the Kaiser Steel Corporation blast furnaces consumed about 1,448 pounds of coke per ton of hot metal produced, compared to the national average of 1,746 pounds.

In 1955, when the national average value of a ton of oven-coking coal at the coking plant was 8.84, the average for eight coke-producing states, including California, was 10.79. In 1955, the national average value of a ton of oven blast furnace coke, f.o.b. plant, was about \$16.30 for coke used by producers; the average value of coke sold to other consumers in four western states (California, Colorado, Texas, and Utah) was \$13.84 per ton. The national average value of oven foundry coke sold in 1955 was \$23.75 and of breeze \$3.48, f.o.b. plants. No blast furnace coke is consumed in California except by Kaiser Steel Corporation, so no local prices are available. The only metallurgical coke sold in California is foundry coke, which in January 1957 cost \$39.30 per net ton delivered, whether from eastern, midwestern, or southern plants. The cost of transporting a ton of coke from Ohio to California was \$11.70 in January 1957. Breeze sold for about \$4.25 per ton f.o.b. midwestern plants in early 1957, with about \$12 per ton additional for rail haulage to California. In early 1957, breeze was sold at Fontana for about \$5.00 per ton, plus local haulage costs, and had a strong competitive position for the limited local market.

## BLAST FURNACE SLAG

Slag is the waste product, principally nonmetallic, that forms in the blast furnace while metallic iron is being recovered from iron ore. Slag, being lighter than the iron, floats as a viscous blanket above the iron, where it absorbs and retains undesirable substances that are removed when the slag and iron are separated.

Blast furnace slag consists mainly of silicates of calcium, magnesium, and aluminum, with smaller amounts of various absorbed impurities, such as sulfur. The calcium and magnesium content of most slags is provided by limestone charged into the furnace; commonly about half a ton of limestone is charged per ton of metal to be produced. The aluminum, siliceous, and less abundant impurities in the slag represent the gangue, or nonferrous portion of the iron ore. The chemical composition of slag is also adjusted by additions of silica (in the form of quartz), and alumina (in the form of clay) when they are lacking in the gangue. An average chemical composition, based upon hundreds of analyses of American blast furnace slags, lists the following substances and percentages: silica 33 to 42; alumina 10 to 16; lime 36 to 45; magnesia 3 to 12; sulfur 1 to 3; iron oxide 0.3 to 2; manganese oxide 0.2 to 1.5; and traces of other elements (Josephson 1949, p. 54).

Physical properties of slag (Josephson 1949, p. 54, et seq.) include the following: bulk specific gravity (dry basis) 2.0 to 2.5; bulk density (crushed, screened, compacted) 75 to 80 pounds per cubic foot; absorptivity 1 to 5 percent; hardness 5 to 6 on Mohs' scale; texture glassy to coarsely crystalline, also scoriaeous. Slag is tough, hard, clean and resistant to wear and crushing; and has a low coefficient of thermal expansion. Its chemical activity ranges from inert to extremely hydric. For many years crushed slag has been recognized as a natural cement, which hardens upon addition of water.

Although slag was long considered to be a waste product of little or no value, a wide variety of uses have been developed for it in recent years. Of about 43 million short tons of slag produced in the United States in 1953 (the latest year for which complete statistics are available) about 71 percent was processed for commercial use (North 1956, p. 2).

Since the early 1800's slag has been used for road surfaces, but now it is used also in macadam, slag concrete and bituminous pavement; as aggregate in reinforced concrete for buildings and bridges; as railroad ballast, roofing granules, aggregate in concrete and lightweight concrete blocks, sewage trickling filter medium, raw material in the manufacture of mineral wool, and ceramic ware (terra cotta), a constituent of portland and slag cements, slag glass, a soil conditioner, and oyster cultch (Josephson 1949).

Blast furnace slag is marketed in the following four classifications: screened air-cooled slag; unscreened air-cooled slag; granulated slag; and expanded slag.

In California, only the Kaiser Steel Corporation at Fontana produces blast furnace slag. It is produced as the unscreened air-cooled type, but it is crushed and screened by another firm before it is removed from Fontana for use.



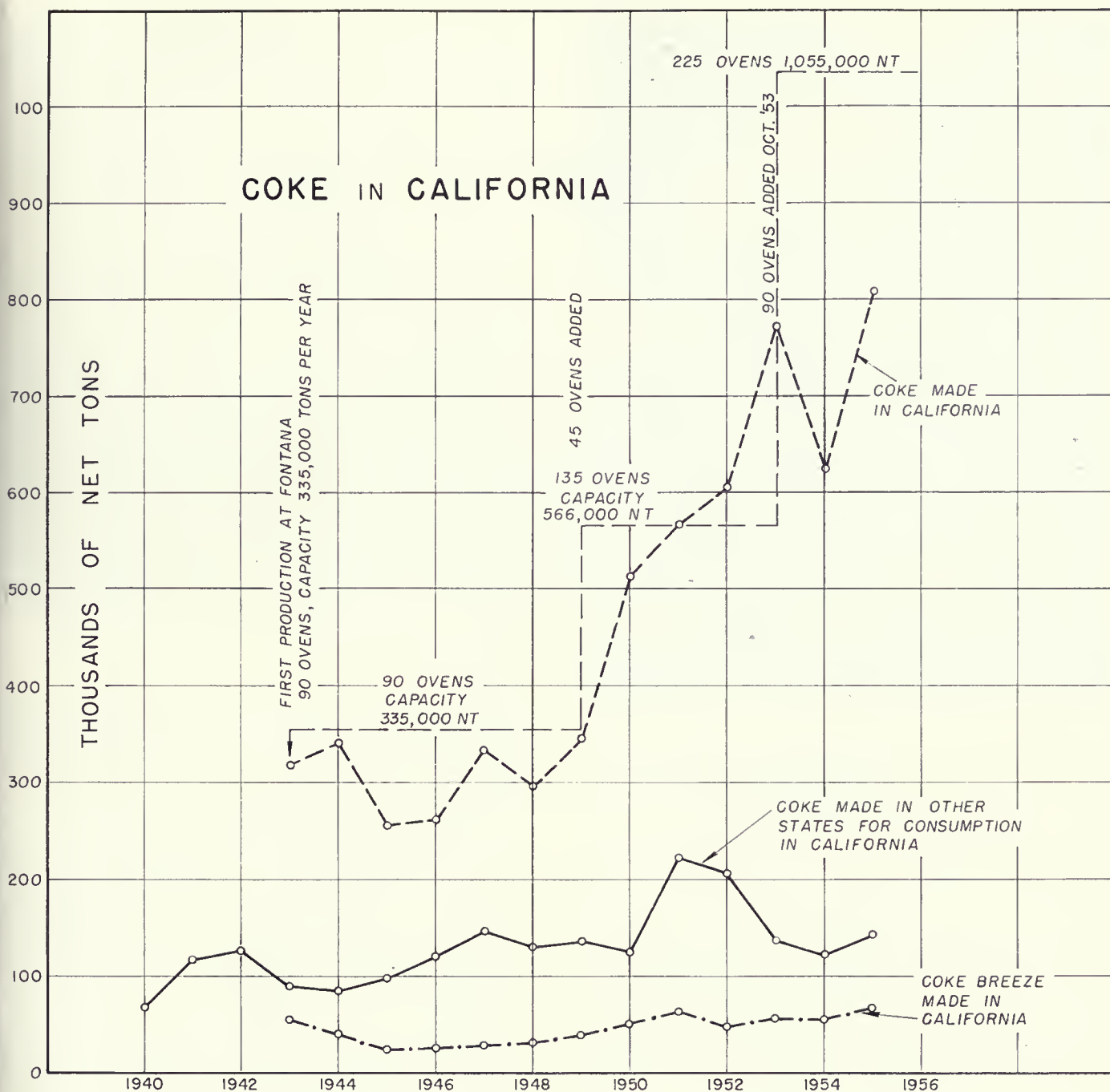


FIGURE 21.

Most of the slag utilized in the United States is used as aggregate, ballast, or fill. When used as aggregate, it increases the resistance of concrete to seawater and fire, and improves stability under conditions of alternate freezing and thawing, and wetting and drying (Josephson 1949). The natural cementing action of slag enables makers of concrete block to use 20 percent less portland cement when slag is used for aggregate. Concrete rocket launching platforms are sometimes made with slag aggregate to resist spalling under the sudden high temperatures of rocket launching. In southern California, sand, gravel, and crushed stone suitable for

ordinary aggregate, ballast and fill are abundant, and less costly to crush and process for these uses than slag.

In 1957, Kaiser Steel Corporation entered a 3-year contract with the California Division of Highways to supply two million tons of slag for use as lightweight fill material on overpasses. Prior to 1957, the principal uses of slag in California were (1) for granules on built-up roofing; (2) as an ingredient in the manufacture of mineral wool, which is widely used for heat-transfer and fireproof insulation; and (3) as aggregate in concrete blocks. Small tonnages were consumed for





FIGURE 22. Discharging a byproduct coke oven at California's only coke plant, which is operated by Kaiser Steel Corporation at Fontana. Red hot coke is being pushed into a special railroad car which will carry it beneath a quenching tower. There water will extinguish and cool the coke, amid spectacular clouds of steam and ash. Coke is then screened: breeze (particles smaller than  $\frac{1}{8}$  inch) is used in the sinter plant; coke is used in the blast furnaces. Photo courtesy of Kaiser Steel Corporation.

road surfacing, track ballast, and aggregate in asphalt and portland cement concrete.

In 1956, about 60,000 tons of slag were consumed in California as granules for built-up roofing, in which alternating layers of tar and roofing felt are finally covered by a protective layer of mineral fragments embedded in tar. Three sizes of granules are used for this purpose:  $\frac{5}{8}$  to  $\frac{1}{2}$  inch;  $\frac{5}{8}$  to  $\frac{1}{4}$  inch; and  $\frac{1}{4}$  to  $\frac{1}{8}$  inch. Slag is desirable for this use because of its comparatively light weight, its porosity which enables it to stick tightly, its opacity to tar-damaging rays of the sun, and its low cost. In 1956, slag granules cost about \$11 to \$12 per ton, bulk, delivered to roofers in the Los Angeles area. The national average price in 1954 for slag granules used in roofing was \$2.20 per ton, f.o.b. plant (North, 1956, p. 4). Because of its light weight, the cost of slag per 100 square foot "square" of roof in southern California was about \$1.00, compared to about \$2.00 for white granules, and \$3.00 for natural-colored granules, in 1956.

In January 1957, three firms in California were making mineral wool; all used slag from Fontana as a principal ingredient. The slag, sized about  $1\frac{1}{2}$  to 2 inches, is remelted to liquid state in cupola and reverberatory furnaces, heated by coke and natural gas, respectively. Various proportions of siliceous gravel and other types

of by-product slags (e.g. phosphate- and borax-rich slags) are added when necessary to increase the silica and alumina content, or to improve other properties of the melt. High-pressure steam directed against a small pouring stream of molten slag disperses and transforms it into innumerable fine filaments known as mineral wool. A thousand pounds of slag yield about 880 pounds of loose mineral wool, which when further processed, yields about 620 pounds of usable material and about 260 pounds of waste (Josephson, 1949, p. 194).

About 35,000 tons of Fontana blast furnace slag have been consumed in California for the manufacture of mineral wool each year since 1950. This material costs between \$2 and \$5 per net ton, delivered in the Los Angeles area. The average price of screened air-cooled slag used for mineral wool in the United States in 1954 was \$1.38 per ton f.o.b. plant (North, 1956, p. 4). Finished mineral wool in the Los Angeles area retailed in January 1957 for \$1.50 per sack (4 cubic feet, granulated); \$65 per 1000 square feet, in paper-backed bats one inch thick; and \$85 per 1000 square feet in bats 2 inches thick.

The waste fraction from mineral wool production consists mainly of tiny globules of "mineral shot," or glassy slag that was not fiberized in the blowing process. Mineral shot is sold in three size grades: "straight-run," about 12- to 60-mesh; "30-mesh," about 18- to 40-mesh; and "50-mesh," about 40- to 60-mesh, for sandblasting use in which it gives about 10 times the service of ordinary sand.

Straight-run shot are used for sandblasting in shipyards, the 30-mesh grade in ordinary sandblasting room practice, and the 50-mesh grade on aluminum and magnesium products to give finer finish. About 10,000 short tons of mineral shot were sold per year for sandblasting in southern California during the early 1950s for prices ranging from \$25 to \$40 per ton delivered. The quantity of mineral shot produced in California fell below the demand in 1956 because of (1) increased use of spinning types of blowing machinery, which make higher quality wool, but a lower proportion of shot than previous types of equipment, and (2) increased use of reverberatory type furnaces in which the shot may be remelted instead of discarded.

A relatively minor tonnage of slag also is produced in both open-hearth and electric furnace steel-making processes, and in other metal-smelting operations. Copper and lead smelter slags are utilized in other states, and have been used in California in past years. The principal use of steel furnace slags in California is at Fontana, where local open-hearth slag is charged into the blast furnaces for its manganese content.

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FIGURE 23. Loading a coarse grade of air-cooled screened blast furnace slag for use in mineral wool at the Fontana yard of Kaiser Steel Corporation.

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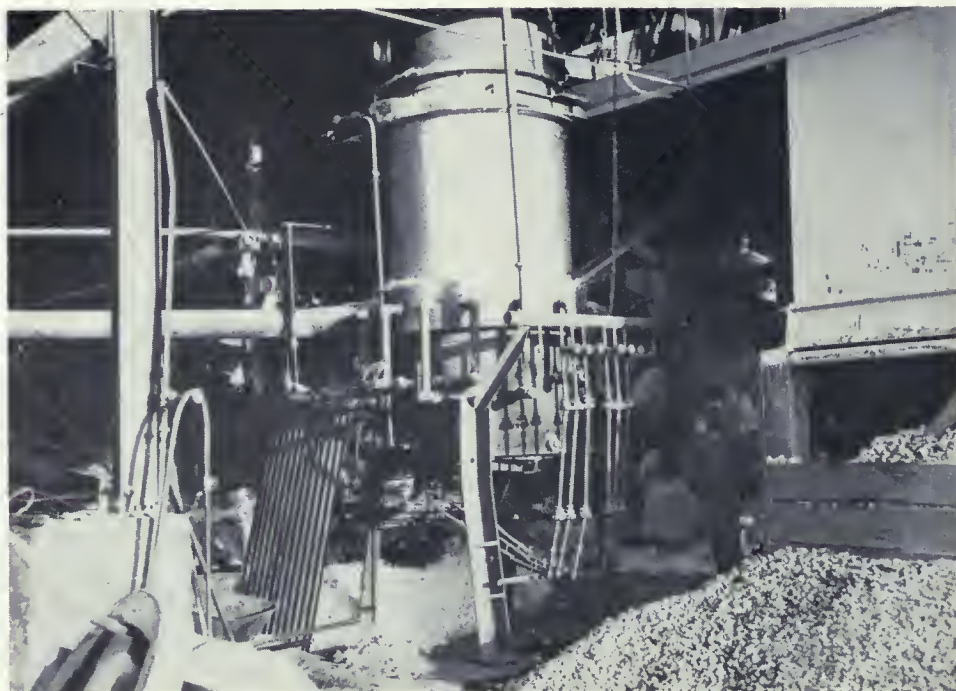


FIGURE 24. Cupola furnace used to manufacture mineral wool at the Fontana plant of Mineral Wool Insulations Company. Pipes leading beneath furnace carry high pressure steam, which blows the molten slag into fibers, away from the viewer. Material at lower right is alluvial gravel which is charged into the furnace, along with slag and coke, to supply silica.



FIGURE 25. Charging scrap metal into one of the three 8000-KVA electric furnaces at the Kaiser Aluminum and Chemical Corporation ferrosilicon plant at Permanente, Santa Clara County, inactive since 1953. Selected scrap iron, coke, and quartz are melted and combined into ferrosilicon by electric energy supplied from the two electrodes which project downward into the furnace hearth (right). *Photo courtesy of Kaiser Aluminum and Chemical Corporation.*



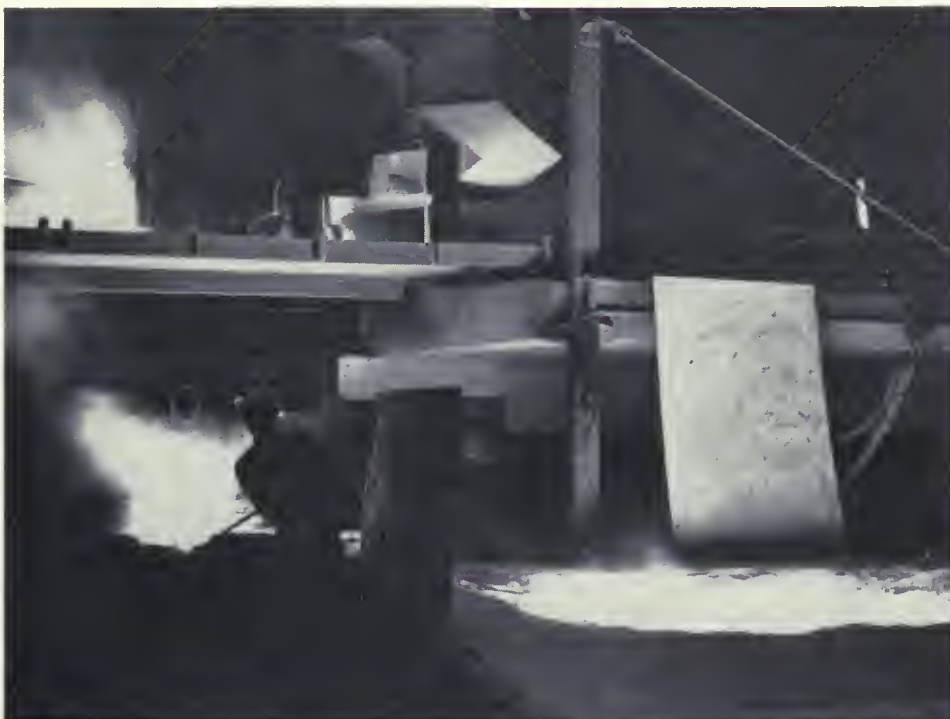


FIGURE 26. Tapping molten ferrosilicon from one of the electric furnaces at the Kaiser Aluminum and Chemical Corporation ferrosilicon plant at Permanente, Santa Clara County. Electrode (upper left) has been raised above the furnace hearth. Molten material flows into sand box (right) where slag is skimmed off before solidification. *Photo courtesy of Kaiser Aluminum and Chemical Corporation.*



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## KYANITE, ANDALUSITE, AND RELATED MINERALS

BY LAUREN A. WRIGHT

Kyanite and andalusite, both of which have been mined in California formally, are members of a group of aluminum silicate minerals that can be used similarly in the manufacture of refractories. The other minerals of the group—sillimanite, dumortierite and topaz—occur in California, but have not been mined commercially here. In an industrial sense, they commonly are referred to as the sillimanite group minerals.

All of the kyanite mined in California has been obtained from a deposit near Ogilby, Imperial County, and all of the andalusite from a deposit in the White Mountains of Mono County (fig. 1). Both deposits were mined nearly contemporaneously from the 1920's to the mid-1940's and have been unworked since. Together they yielded a total of about 36,000 tons of aluminum silicate rock, but in 1955 they remained idle largely because no ready market existed for the kyanite and because most of the known bodies of higher grade and easily recovered andalusite had been removed.

*Mineralogy, Geology, and Out-of-State Occurrences.* Andalusite, kyanite, and sillimanite are identical in chemical composition ( $\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ ), but have different crystal structures. These three differ in chemical composition from dumortierite ( $8\text{Al}_2\text{O}_3 \cdot \text{B}_2\text{O}_3 \cdot 6\text{SiO}_2 \cdot \text{H}_2\text{O}$ ) and topaz ( $2\text{Al}_2\text{O}_3 \cdot 2\text{Al}(\text{F} \cdot \text{OH})_3 \cdot 3\text{SiO}_2$ ) principally in the presence of volatiles in the latter two. Each of the five has a vitreous to subvitreous luster, specific gravities that lie in the range of 3.1 to 3.7, and a moderate range of colors. Reddish tints are characteristic of andalusite; kyanite is commonly blue; most sillimanite is gray; topaz is generally colored tints of yellow to white or gray; and blue, greenish blue, or violet characterize dumortierite. Kyanite is generally distinguishable from the other four by a bladed habit and by two hardnesses, one of 4 (on the Mohs' scale) parallel to the length of the blade, and the other of 7 parallel to the width. Andalusite, sillimanite and dumortierite have hardnesses in the range of 6 to 7.5 and prismatic habits. Topaz is prismatic and has a hardness of 8. Although the properties cited above are helpful in field determinations, these minerals are best identified by optical methods.

Andalusite, kyanite, sillimanite, and dumortierite are most common in metamorphosed sedimentary rocks. In some places the original sediments appear to have been predominantly argillaceous; but most of the deposits of commercial interest appear to have developed from clay-rich quartzites. Locally these minerals occur within or associated with pegmatite dikes or other bodies of granitic rocks. Some deposits are partly or wholly of contact-metamorphic origin. Quartz veins associated with andalusite- and kyanite-bearing rocks also commonly contain these minerals. Topaz is most abundant in acidic igneous rocks and is locally a constituent of metamorphosed sedimentary rocks.

The most extensively mined of the domestic kyanite deposits are in the southeastern United States. Here a belt of crystalline rocks, which extends from Virginia to Alabama, contains deposits of disseminated kyanite whose total reserves are believed to be measurable in tens of millions of tons. The kyanite occurs in quartz-rich

metamorphic rocks, generally in proportions of 20 to 30 percent. In recent years, two operations—one near Clover, South Carolina, and another near Farmville, Virginia—have been the source of all of the kyanite produced in the United States. Several hundred tons of kyanite concentrates from these operations are shipped into California annually.

The world's highest quality kyanite, which is obtained from northern India, occurs as massive segregations in quartz-kyanite rock. It is mined in the form of residual boulders that have weathered from bedrock and lie on or near the surface of the ground. The mined material consists essentially of kyanite and about 10 percent corundum and contains 55 to 59 percent  $\text{Al}_2\text{O}_3$ . It requires no beneficiation and is used in the manufacture of high-strength refractories. Kyanite of comparable grade has been noted in Virginia, but apparently is not in commercial quantities (Gunsallus, 1955).

Outside of California, the only domestic production of andalusite on a commercial basis was a small tonnage mined in 1949 from deposits near Hawthorne, Nevada. In these deposits, andalusite and other high-alumina minerals occur in bodies in metavolcanic rock. The mineralization is most intense along schistose shear zones. The 1949 output consisted of about 3,000 tons which was shipped to the Technical Porcelain and Chinaware

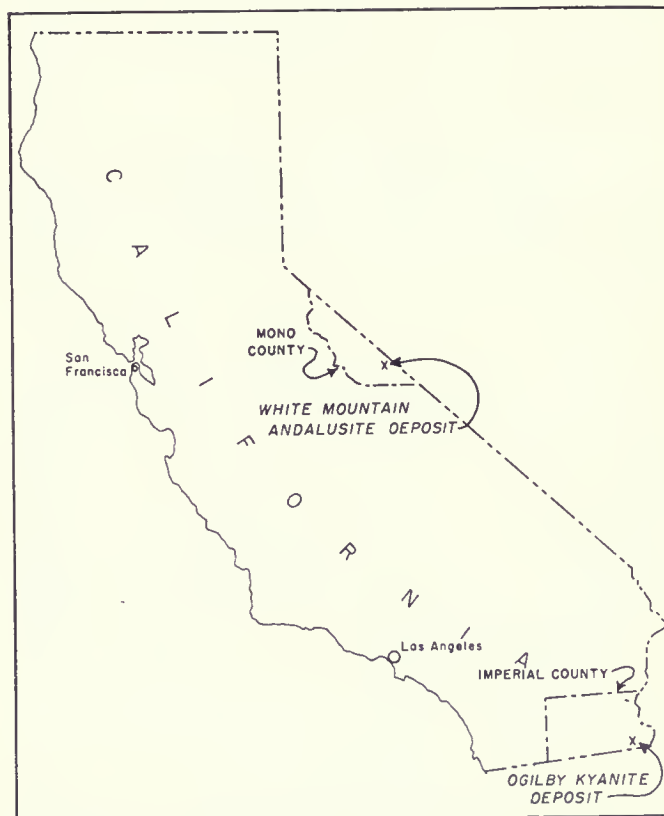


FIGURE 1. Index map of California showing locations of the White Mountain andalusite deposit in Mono County, and the Ogilby kyanite deposit in Imperial County.



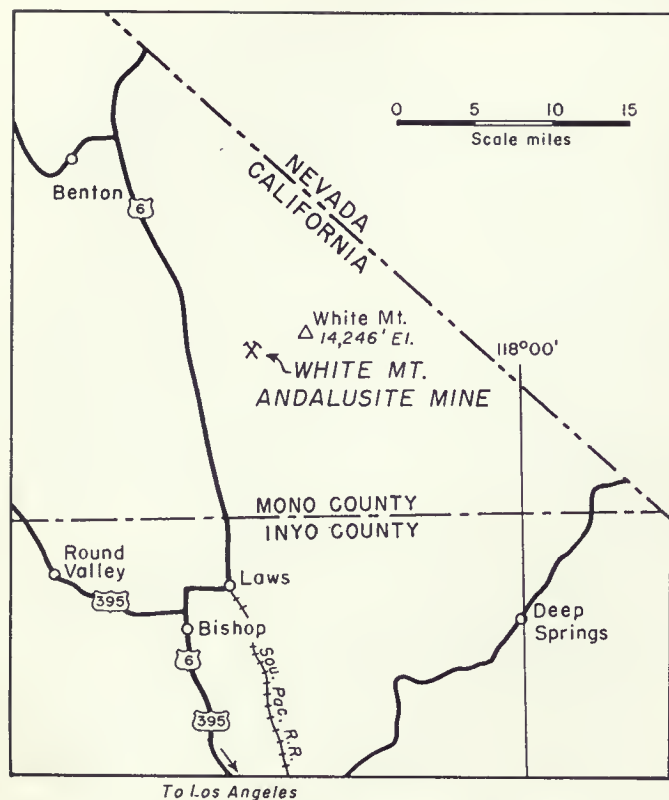


FIGURE 2. Index map of parts of Mono and Inyo Counties, showing location of White Mountain andalusite mine.

Company in El Cerrito, California (J. D. McLenegan, personal communication, 1955).

Dumortierite segregations in quartz-sericite schist near Oreana, Nevada, have been the only commercial source of this mineral in the United States but have not been worked in recent years. Small tonnages of topaz were produced in South Carolina in the period 1939-1945.

**Localities in California.** Nearly all of the andalusite mined in the United States has been obtained from the previously noted White Mountain area in Mono County, and about 18 miles north of Bishop (fig. 2). The andalusite deposits\* are confined to a zone in a structurally complex terrane of metamorphic rocks — principally quartzite, sericite schist, and metaporphry — of undetermined age. The whole is intruded by Mesozoic quartz monzonite. The andalusite-bearing zone trends roughly northward, is several miles long and probably averages no more than a mile in width. Within the zone the andalusite deposits are discontinuous and irregularly distributed, and only locally have they proved large enough and rich enough to warrant economic development. Most of the deposits occur within or marginal to large, elongate bodies of quartzite that range from a few hundred feet to 1200 or more feet in exposed width. Some lie within schist that borders the quartzite.

Most of the andalusite rock mined in the White Mountains area has been removed from a deposit on a single

claim which lies at an average elevation of about 9,000 feet and has been developed by workings known as the Vulcanite mine (fig. 3). Here the andalusite rock was found to occur in a layer much of which was exposed on and attached to a steep, east-facing cliff of quartzite. This layer was 5 to 20 feet thick, about 400 feet long, and 100 feet in vertical dimension, and appeared to lie along a pre-mineral fault. Andalusite also was removed from irregular bodies that extended for as much as 100 feet from the outer layer into the cliff and apparently were fracture-controlled. Sharp contacts exist between the andalusite rock and the bordering quartzite.

The Vulcanite workings, which consist mainly of steep, closely connected stopes, yielded a total of about 20,000 tons of hand-cobbed rock that contained 53 percent or more of andalusite. For several years the minimum acceptable grade was held at 81 percent. By determination of the specific gravity of the ore a reasonably accurate control of the andalusite content was maintained at the mine. This control was based upon the difference in specific gravity between andalusite (sp. gr. 3.20) and quartz (sp. gr. 2.66), the principal impurity. The hand-cobbed material was carried  $4\frac{1}{2}$  miles on muleback, and then trucked an additional three miles to a stockpile.

With the depletion in the late 1930's of the known mineable reserves at the Vulcanite mine, operations were transferred to bodies known as the "diaspore veins" which lie about 1,000 feet west of the Vulcanite workings and are exposed nearly 1,000 feet lower. These veins, which occur along a quartzite-schist contact as well as within the schist, have been emplaced along faults that dip eastward to northeastward (fig. 3). They contain high-grade lenses of diaspore accompanied by various proportions of rutile and pyrophyllite. The diaspore appears to be an alteration of andalusite of which only traces remain in most of the lenses. Most of the diaspore-rich rock has been removed from bodies along a 1,000-foot segment of a single vein. Workings consist of several short adits at different elevations and small stopes and raises. Diaspore rock was the last material to be mined and was used in the same manner as the andalusite. The last of the diaspore stockpile was removed in the mid-1950's.

The largest body of andalusite-bearing rock in the mine area lies about 3,500 feet southwest of the Vulcanite mine and on the opposite side of a deep canyon. This body, known as the Vulcanus No. 8, averages about 40 percent andalusite at the surface and was not mined extensively. It is about 600 feet long and 230 feet wide in the outcrop; the depth to which it extends is unknown.

Other occurrences of andalusite are widespread in California (Murdoch and Webb, 1948, pp. 47-48), but none of those noted to date are as rich as the White Mountain deposit. In most of the other deposits, the andalusite is disseminated in metamorphic rocks. The best known of these are the occurrences in Madera County of well-developed crystals of the variety chialiolite. Andalusite-bearing pegmatites have been noted in Fresno and Riverside Counties, and the mineral also has been noted in a quartz vein in San Diego County.

The kyanite deposits of Imperial County, the only source of commercial kyanite in California to date, are in the southwestern part of the Cargo Muchacho Mountains and about 3 miles north of the Ogilby rail siding

\* Most of this description has been abstracted from the following unpublished report: Lemmon, D. M., *Geology of the andalusite deposits in the northern Inyo Range, California*: Stanford University Ph.D. thesis, 70 pp., 1937.



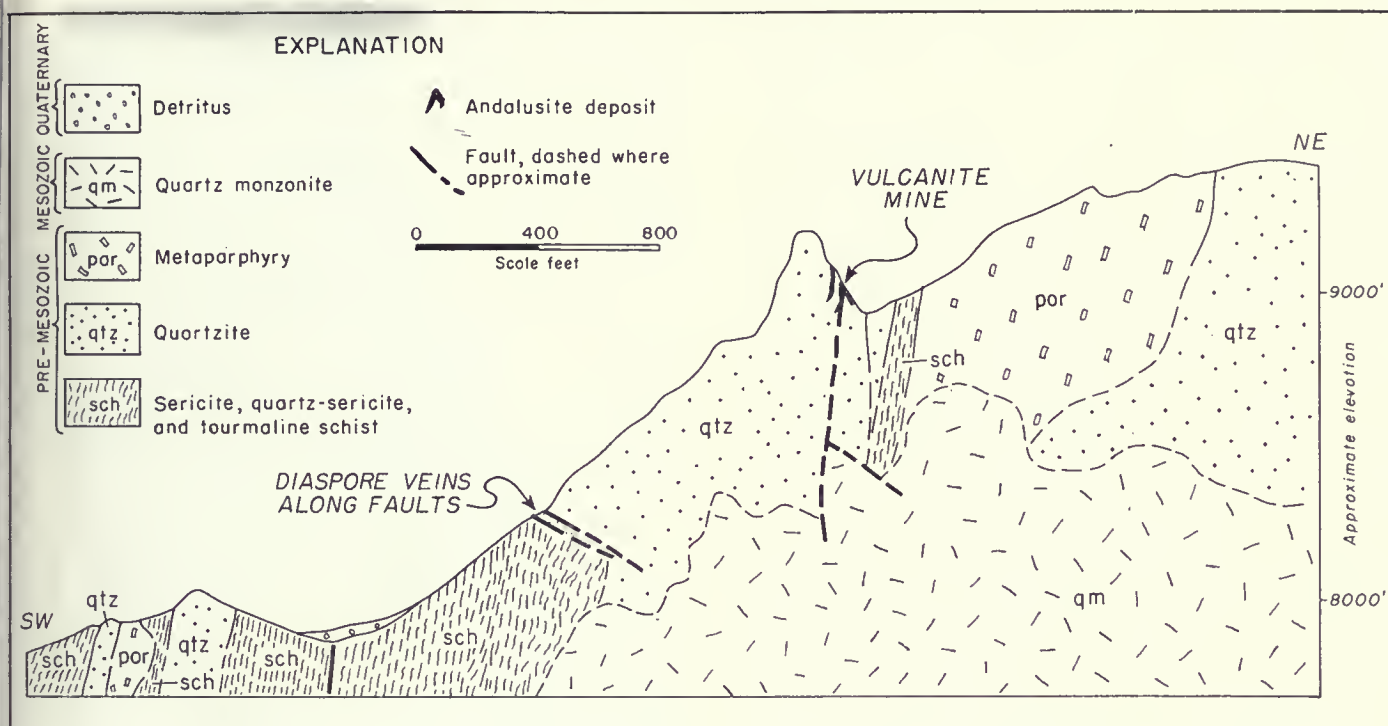


FIGURE 3. Generalized geologic cross-section through White Mountain andalusite-bearing area. After D. M. Lemmon, 1937.

(fig. 4). In a geologic setting somewhat similar to that of the White Mountains andalusite, the Ogilby kyanite occurs as clusters of blue blades that are disseminated through much of the quartz-rich part of a layered and highly metamorphosed pre-Mesozoic formation (Henshaw, 1942). The quartz-kyanite rock, which locally contains abundant limonite, is discontinuously exposed for a distance of about 1 mile along the west face of the mountains and locally appears to be as much as 400 feet thick. Virtually all of this rock contains kyanite in excess of 15 percent. The mined material is said to have averaged 35 percent or more kyanite and large tonnages of this grade of rock apparently remain.

The mining was confined largely to a single hill where a steeply dipping, kyanite-rich mass, with a maximum thickness of about 400 feet, has been developed (fig. 5). The kyanite rock was removed from benches in a large open cut that was about 140 feet high and 100 feet in average width (fig. 6) when the operation was shut down in 1946. The presence of quartz veins and masses of kyanite-poor quartzite required that the mining be somewhat selective, but only a small part of the kyanite-rich mass was removed during this operation. The rock was sorted, trucked 2 miles to Ogilby siding, and hauled by rail to Los Angeles for treatment. Other bodies that apparently are comparable to the developed one are exposed in the area, but have not been worked. Muscovite-schist forms part of the same formation and for many years has been mined in a separate operation (see section on mica in this volume).

**Utilization and Treatment.** The usefulness of kyanite, andalusite and the related minerals is based upon their conversion when heated to temperatures in the range of 2000° F. to 3000° F., to a mixture of mullite

( $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ ) and free silica. As mullite is stable to 3290° F., has a low thermal expansion, is chemically inert, and has high strength, it is valued as a constituent of refractories.

The mullite-silica mixtures thus produced differ in their texture, density and relative proportions of mullite and silica, depending on the minerals used and their textural and crystallographic features. Andalusite, for example, shows little volume change when calcined,

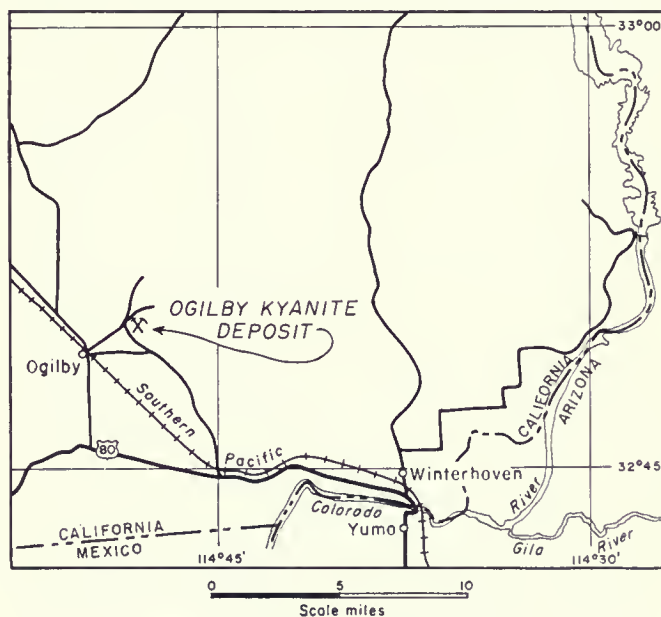


FIGURE 4. Map showing location of Ogilby kyanite deposit, southeastern Imperial County, California.



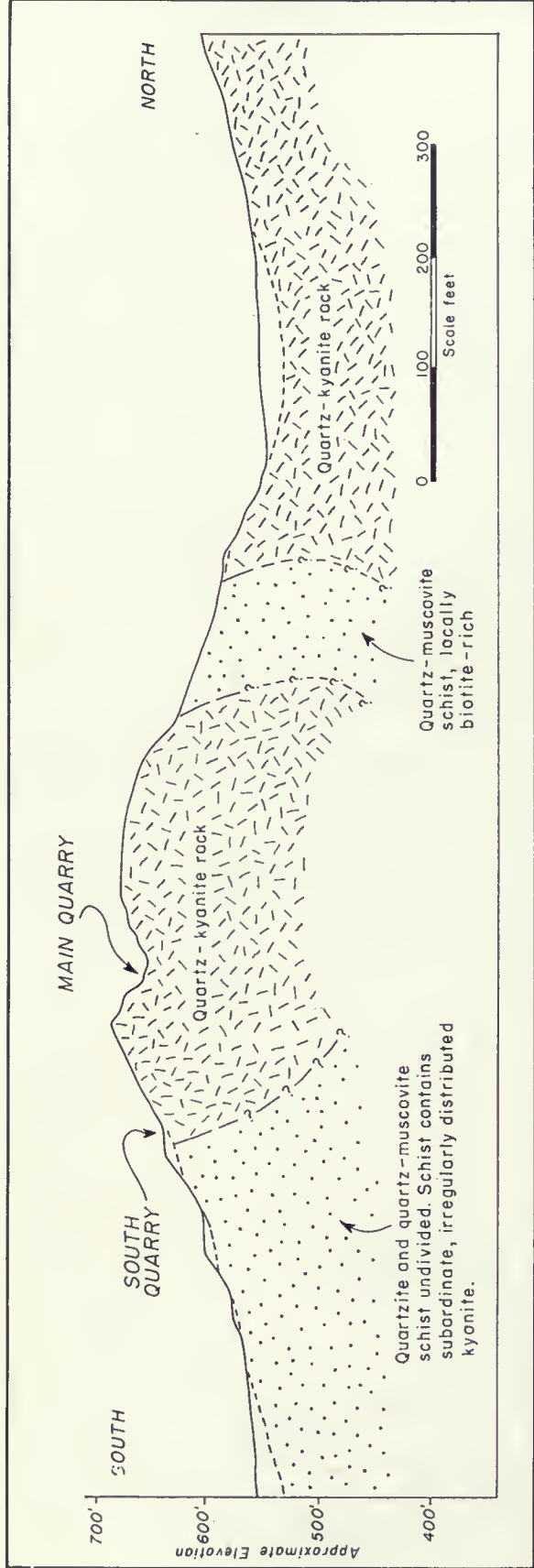


FIGURE 5. Geologic cross-section through part of the Ogilby kyanite-bearing area. *Geology by Ian Campbell and L. A. Wright.*



FIGURE 6. View northeast toward main quarry in Ogilby kyanite area. Cross-section in figure 5 extends, nearly parallel to page, through upper part of hill.



whereas kyanite expands markedly. The bladed kyanite, characteristic of domestic deposits, also cracks and exfoliates to produce a volume increase of as much as 200 percent; whereas Indian kyanite, which is massive, calcines to a much harder and less porous material. Moreover, domestic kyanite must be rather finely ground for beneficiation, whereas Indian kyanite is available in much coarser form. The usefulness of domestic kyanite in refractory manufacture is, therefore, more restricted than that of Indian kyanite. Much of the domestic output is used in refractory cement.

Mullite-silica mixtures also can be produced by sintering or fusing a mixture of silica and various aluminous materials such as alumina, bauxite, or diaspore clay. The product is known as synthetic mullite. With synthetic mullite, as well as with mullite obtained by calcining minerals of the sillimanite group, the quality of the manufactured refractory depends largely upon the size and density of the grains.

Most mullite refractory bodies are manufactured by bonding mullite of specified size and density, then power pressing it into bricks and shapes and firing it in one of several types of kilns. Some bricks and shapes are formed by hand.

Champion Sillimanite, Inc., which operated the White Mountain mine, used the andalusite as a raw material in the manufacture of refractories and high-grade porcelain for spark plugs and chemical ware. The andalusite-bearing rock was shipped to the Detroit plant of the Champion Spark Plug Company, where it was crushed, ground, and treated magnetically to remove the iron. In the manufacture of refractories it was screened to minus 8 mesh and mixed with electrically fused alumina. For porcelain manufacture the andalusite was mixed with fluxes, clays, dumortierite and water and reground to minus 325 mesh. The mixture was again treated magnetically, and then sent through a filter press, molded, and fired at a temperature of 2715° F. (Riddle and Foster, 1949).

Kyanite from the Ogilby deposit, which was operated by the Vitrefrac Corporation of Los Angeles, was also used in the manufacture of refractories. The kyanite-quartz rock was heated to a temperature of 1700° F. to 1800° F. in a rotary kiln. Iron oxide was thus chemically reduced to allow a later magnetic separation. Alpha quartz was converted to beta quartz by this heating and again became the alpha variety by a quenching in water.

The sudden expansion and contraction of the quartz, with but slight volume change in the coarser kyanite caused a separation of the two minerals. Subsequent crushing, followed by washing over slightly inclined shaking screens, allowed removal of the quartz and retention of relatively pure kyanite blades. A mixture composed of the kyanite separate and other high-alumina material was then fused in an electric furnace. The final composition approximated that of mullite ( $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ ). The Vitrefrac Corporation, however, was liquidated in 1946 and the Ogilby deposit has since been idle.

The kyanite-producing concerns in the southeastern United States have employed rather complex flow sheets that involve (1) preliminary grinding or disintegration, (2) screening, (3) electromagnetic treatment, (4) float-

tion, (5) calcining at 1480° C. in a rotary kiln, and (6) grinding to sizes in the range of minus 32 to minus 200 mesh. The concentrates contain 90 percent or more kyanite.

The term "high-alumina" refractories is ordinarily applied to those that are composed largely of mullite and contain at least 47.5 percent  $\text{Al}_2\text{O}_3$ . High-alumina refractories are graded according to their  $\text{Al}_2\text{O}_3$  content, which exceeds 90 percent in the highest grade; and, according to their pyrometric cone equivalents, which range from 34 to at least 38 with corresponding temperatures from 3200° F. to at least 3335° F. Because high-alumina refractories are more expensive than refractories made from fire clays, they are used only in refractory bodies for which the specifications for strength, durability and resistance to slag are unusually high. Such bodies, which constitute about 7 percent of the total volume of refractories manufactured in the United States, are especially important in the metallurgical, glass, ceramic, and cement industries. The bodies consist principally of liner blocks and fittings for types of kilns and furnaces, and of kiln furniture for the ceramic industry. Nationally, the metallurgical industries consume about 50 percent of the domestic output of high-alumina refractories and the glass industry about 40 percent. The ceramic industry is the principal consumer of the remaining 10 percent (Gunsallus, 1955).

Before World War II, Indian kyanite was the principal mullite-forming raw material used in the manufacture of high-alumina refractories. The uncertainty of the Indian supply, however, hastened the development of synthetic mullite which is now used to produce refractories that are comparable in price and comparable or superior in quality to those made from Indian kyanite. Consequently, the imports of Indian kyanite into the United States dropped from 10,370 tons in 1951 to 4,835 tons in 1952 (Gunsallus, 1955).

In 1955, the volume of high-alumina refractories consumed annually in California was estimated at slightly more than 1.5 million "9-inch equivalent,"\* the manufacture of which required about 9,000 tons of high-alumina materials mostly in the range of 50 to 70 percent  $\text{Al}_2\text{O}_3$  (McLenegan, 1956). Of this tonnage, about one-third was used in the manufacture of refractories for California's glass industry, about one-third for its cement industry and about one-fifth for its iron and steel industry. About 80 percent of the volume of high-alumina refractories marketed in California, however, was being manufactured in the eastern United States, so that the state's refractory industry offered a small market for high-alumina materials.

*Markets and Prices.* In 1955, several hundred tons of domestic kyanite were being used annually in California for the manufacture of kiln furniture for the ceramic industry. This constituted the only ready local market, known to the writer, for any of the sillimanite group minerals, and the tonnages involved appeared too low to support the mining and beneficiation of material from local deposits.

A survey by the U. S. Bureau of Mines (J. D. McLenegan, 1956) indicates that the potential market for sillimanite group minerals in California and Nevada

\* A 9-inch equivalent is the volume of a 9-inch brick or 100 cubic inches.



is about 10,000 tons annually, provided that the high-alumina refractories consumed in this region were manufactured locally and the minerals also were used to up-grade ordinary fireclays. With an adequate local source of such minerals, this survey suggests that the demand could rise to as high as 40,000 tons. However, this market would have to be met by material containing 50 to 80 percent  $Al_2O_3$  and much of it would have to have physical properties similar to those of Indian kyanite or synthetic mullite. Kyanite of the type mined and beneficiated in the southeastern United States, and to which the Ogilby kyanite appears comparable, probably would be satisfactory for only a relatively small proportion of this potential market.

The prospective producer of sillimanite group minerals in California, therefore, must secure local markets that are yet largely undeveloped, be able to compete with the producers of synthetic mullite, and maintain a source of high-quality raw material. Future developments in high-alumina technology, however, may lead to an expanded market for the materials available in California and to a renewal of the mining of sillimanite group minerals in the state. If so, the marketing of the local products would be favored by the cost of shipping high-alumina materials from eastern states.

Most of the domestic kyanite consumed in California is purchased in earload lots at plants in South Carolina and Virginia. At these plants the following prices pertained in 1956: 35 mesh material in earload lots, \$29 per ton bulk and \$32 per ton bagged; 200 mesh material in earload lots, \$40 per ton bagged. Imported kyanite, 60 percent grade, was being delivered in bags at Atlantic ports for \$76 to \$81 per ton.\*

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## LEAD

BY RICHARD M. STEWART

Deposits in California have yielded a total of nearly 450 million pounds of lead from 1877 through 1954. This output represents about eight-tenths of one percent of the total mine production of recoverable lead in the United States for the same period. During the decade ending with 1954, the annual production of lead in California ranged from a low of 2,671 tons in 1954 to a record high of 15,831 tons in 1950. Mines in Inyo County have been the principal sources of lead in California.

*Mineralogy and Geology.* The primary mineral galena ( $\text{PbS}$ ) is the chief source of lead throughout the world, but the secondary minerals, anglesite ( $\text{PbSO}_4$ ) and cerussite ( $\text{PbCO}_3$ ), also are significant ore minerals in the oxidized zone of some deposits. Other significant, although less abundant, minerals in the oxidized zone of lead deposits are: those of the pyromorphite series [ $\text{Pb}_5(\text{PO}_4, \text{AsO}_4)_3\text{Cl}$ ]; linarite, a basic sulfate of lead and copper; plumbo-jarosite [ $\text{PbFe}_6(\text{OH})_{12}(\text{SO}_4)_4$ ]; and wulfenite ( $\text{PbMoO}_4$ ). Zinc and silver minerals commonly are associated with lead minerals in California as well as throughout the world. (See sections on silver and zinc in this bulletin). Primary lead-zinc deposits typically occur as cavity fillings or replacement bodies and occur mostly in limestone or dolomite. Most lead-zinc deposits clearly are associated with intrusive igneous rocks.

In the oxidized zone—which lies above the water table and in which oxygen and water react upon minerals and rocks—galena alters to anglesite which in turn alters to cerussite. A fragment of lead ore thus oxidized may consist of a core of unaltered galena surrounded by roughly concentric alteration zones, grading outward through anglesite to cerussite. Anglesite and cerussite are relatively insoluble, and lead ore is the most resistant of all base metal ores to further chemical alteration. Under particularly favorable oxidizing conditions, lead may be leached slightly but not enough to affect the grade of the ore appreciably for more than a few feet below the surface.

In the oxidized zone, however, enrichment can take place by leaching of sulfur, zinc and iron and possibly other constituents from the ore. This was the principal process in the formation of the high-grade lead-silver ores that were first mined from the deposits in the Cerro Gordo and Darwin districts in California. All of the lead deposits in California have been considerably oxidized, but primary sulfide minerals are present, in minor to major proportions, in all of them. As workings extend deeper into a deposit to zones where oxidation is less complete than at higher levels, the primary sulfides become the most abundant ore minerals.

*Localities in California.* Most of the lead produced in California has been obtained from three districts, each of which is in Inyo County. These are (1) the Cerro Gordo district, about 13 miles east of Lone Pine and near the crest of the Inyo Range; (2) the Darwin district, about 35 miles southeast of Lone Pine; and (3) the Tecopa district, at the southern end of the Nopah Range in the southeastern corner of Inyo County.

The Cerro Gordo mine, which ranks second to the Darwin mines as a source of lead in California, has a total output with an estimated value of \$15,000,000. The Cerro Gordo district is credited with ore valued at \$17,000,000. The Cerro Gordo mine has yielded about 150,000 tons of ore, including about 115,000 tons of high-grade lead-silver ore and 32,000 tons of oxidized zinc ore. Most of the lead ore contained 40 percent lead and a high proportion of silver; the oxidized zinc ore contained 35 to 40 percent zinc (Carlisle and others, 1954, p. 42). The Cerro Gordo mine, although worked intermittently until the late 1940's (Norman and Stewart, 1951, pp. 58-59), has not been a significant source of lead since 1877.

The host rocks for the ore bodies in the Cerro Gordo district are limestone, marble, and quartzite beds that comprise the Cerro Gordo limestone of Devonian age. The major structural feature in the mine area is a highly faulted anticlinal fold; the Devonian and overlying Carboniferous rocks have been intruded by two small stocks of monzonite porphyry and by dikes of monzonite porphyry, diabase and quartz-diorite porphyry, in that order (Carlisle et al., 1954, p. 43).

The ore bodies, all nearly vertical, south-plunging, chimney-like bodies, were distributed, according to Knopf (1918, p. 113), through a north- to northwest-trending zone 1,500 feet long and several hundred feet wide. Horizontal dimensions of individual bodies were small, but the ore shoots were fairly persistent vertically. The Jefferson stope, on the most southeasterly ore body, was 3 to 20 feet wide, 70 feet in average length and 1,000 feet or more in vertical dimension. The China Stope (Union) ore body, 800 to 950 feet north of the Jefferson body, ranged in width from 15 to 40 feet, was as much as 100 feet long, and was mined through a vertical range of about 550 feet. These two ore bodies were the largest encountered by the Cerro Gordo workings, although four other ore bodies were large enough to have been mined and named individually.

The ore minerals are argentiferous galena, cerussite, anglesite, smithsonite, sphalerite, tetrahedrite, and pyrite. Much of the zinc in the lead-rich deposits was removed in solution and formed secondary deposits. Zinc ore, composed principally of smithsonite and commonly very high in grade, was found in pipes and irregular masses that lay on the footwall side of the lead deposits. This zinc ore was mined separately during the period 1911-15.

The principal opening of the Cerro Gordo mine is the 900-foot Belshaw shaft with levels at 85, 200, 400, 550, 700 and 900 feet. Winzes from the 900-foot level connect to level workings at 1,000, 1,030, 1,100 and 1,150 feet. The underground workings total more than 15 miles in length.

The ore bodies of the Darwin district were discovered in 1874 and in recent years have been the principal source of lead in California. They occur in Pennsylvania limestone which is folded about northeasterly to northwesterly axes. The major structural feature is a northwestward-plunging anticline, the axis of which lies



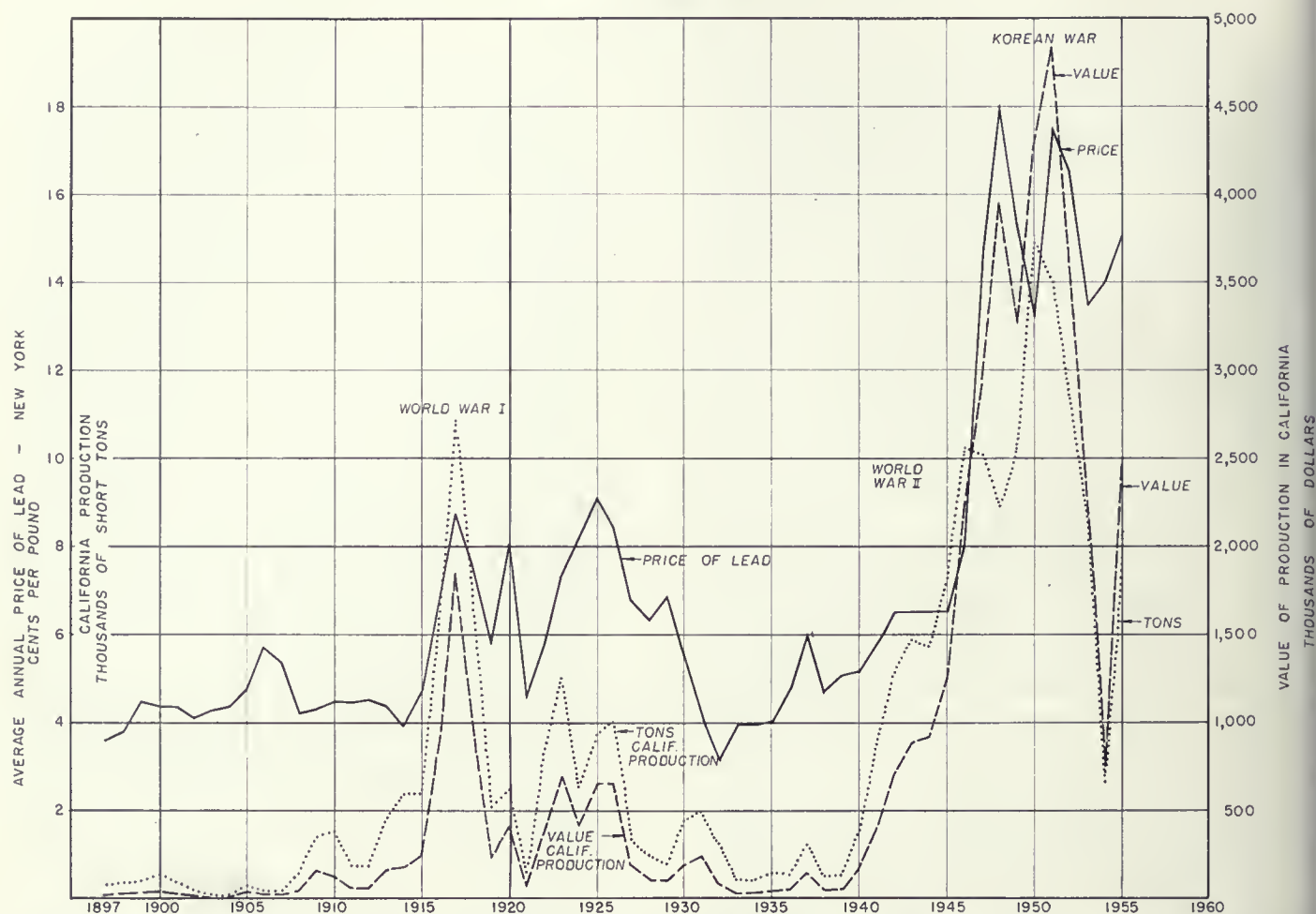


FIGURE 1. Chart showing amount and value of lead produced in California and annual average price—New York—for lead, 1897-1955. (Data from Averill, C. V. and others, 1948, *California mineral production for 1946*; California Div. Mines Bull. 139, p. 45; U. S. Bureau Mines, various issues, Mineral industry surveys; Eng. and Min. Jour., various issues, Metal and mineral markets.)

near the crest of the Darwin Hills. The limestone has been silicated in a wide zone peripheral to a quartz diorite stock that was intruded mainly along the core of this anticline and for an exposed distance of about 5 miles.

Mineralization is mesothermal, related to the quartz diorite, and has been guided by igneous contacts, bedding planes and cross fractures. "In order of importance, the orebodies are: (1) bedded replacements that commonly are more or less localized along anticlinal flexures, and lie near but not in contact with the intrusive sills; (2) irregular replacements of the silicated limestone along fissures; and (3) fissure fillings" (Carlisle et al., 1954, p. 45).

The principal ore bodies lie in two groups along or near the west side of the quartz diorite stock. One group is mined through the Defiance group of workings; the other group lies 1,500 to 2,000 feet north and is mined through the Thompson and Independence workings. The Defiance, Thompson, and Independence mines formerly were operated through adits and inclined shafts. All the workings now are connected to the Radiore tunnel, also known as the 400-level. The ore-bearing zones have been explored and mined through a vertical range of about 750 feet. Most of the workings in the Defiance mine are

confined to a block roughly 700 feet square in horizontal section. The Thompson and Independence workings are contained in an elongate block, about 1,500 feet long and 500 to 900 feet wide (Norman and Stewart, 1951, pl. 2).

The major primary sulfides are argentiferous galena and sphalerite. Minor to very minor proportions of pyrite, chalcopyrite, tetrahedrite, bornite, chalcocite and covellite are present. Extensive but irregular oxidation has produced cerussite, anglesite, plumbo-jarosite, sooty argentite and cerargyrite. Leaching of zinc, sulfur and some iron has been important in the residual enrichment of the oxidized ore (Davis and Peterson, 1949, p. 138). The deposits also contain numerous rare minerals and mineral associations. During World War II, the Darwin mine yielded several hundred tons of high-grade oxidized lead-silver ore that contained 10 to 15 percent  $\text{WO}_3$ , much in the form of well-developed scheelite crystals.

Little has been published concerning the size of individual ore bodies, but Davis and Peterson (1949, pp. 139-142) describe a disc-shaped ore body 40 feet thick at mid-section and about 150 feet in maximum dimension. Ore extracted from this body totaled about 40,000 tons. A large ore body in the Essex ore zone of the Thompson and Independence group was mined down-



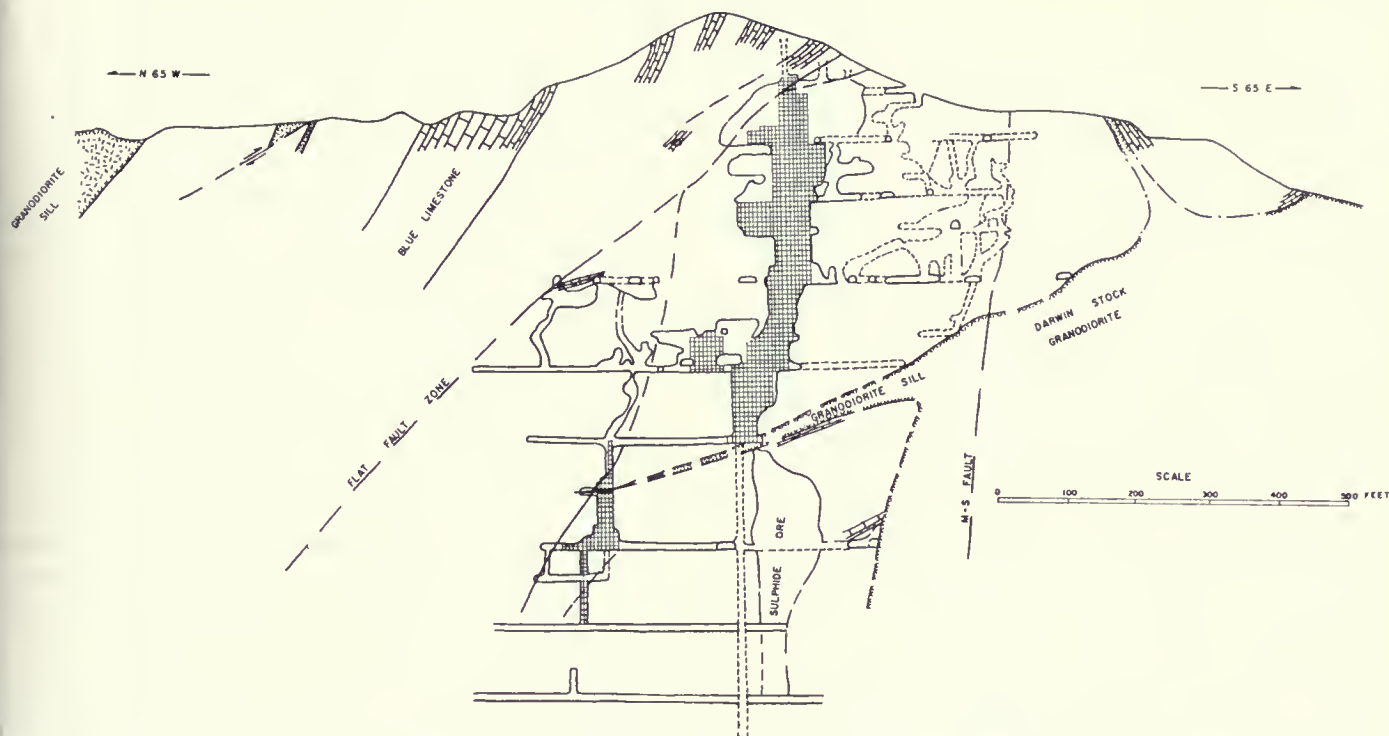


FIGURE 2. Longitudinal section of the Essex region, Thompson and Independence group, Darwin Mines. After Davis and Peterson, 1949.

ward for about 500 feet from the surface, along a strike length of about 50 feet, and across a width of about 20 feet (Davis and Peterson, 1949, p. 142).

Shipping-grade ore, possibly 15 percent lead or higher in grade, constitutes less than 10 percent of the ore mined and is mostly oxidized material. Lower-grade ore is treated in the 350-ton concentrating plant at Darwin. Mill heads average 6 percent lead, 7 percent zinc and 5 ounces of silver per ton (Huttl, 1953, pp. 81-83). Oxide ore, which is concentrated in a separate mill circuit, averages 7 percent lead.

The value of the total production of the principal mines in the Darwin group to 1953 is estimated to be about \$25,000,000. This can be broken down as follows: \$3,000,000 prior to 1900; \$4,000,000 between 1900 and 1945 when the Anaconda Copper Mining Company purchased the property; and \$18,000,000 between 1945 and 1953 (Carlisle et al., 1954, p. 44). From August 1945 to March 1954, about 100,000,000 pounds of lead, 44,000,000 pounds of zinc, and 5,600,000 ounces of silver were recovered (Kildale, M. B., 1954, personal communication). Early in 1954, a drop in the price of lead and zinc caused the operations at Darwin to be discontinued, but they were resumed in 1955.

Nearly all the lead ore from the Tecopa district has been produced from several mines that are consolidated as the Anaconda Copper Company's Shoshone mines. The host rock for all the ore bodies is the Noonday dolomite of Lower Cambrian (?) age. This formation lies unconformably upon pre-Cambrian metamorphic and sedimentary rocks and is overlain by other Lower Cambrian (?) sedimentary rocks. The ore bodies were formed along the Shoshone fault vein (Carlisle, et al., 1954, p. 46) which trends northwest. The largest ore bodies appear to

have formed at junctions of the Shoshone fault with cross fractures and faults.

Most of the ore in each of the deposits is highly oxidized. Cerussite and anglesite are predominant, and are associated with iron oxides, smithsonite, calamine, linarite, and caledonite. Residual galena, pyrite, and sphalerite are present in minor proportions.

The principal mines of the Shoshone Mines group are: the Noonday; the Columbia, which lies about a quarter of a mile to the southwest on a faulted segment of the Shoshone vein; and the War Eagle, which lies about two-thirds of a mile southeast of the Noonday. The Gunsight mine, about 2 miles northwest of the Noonday, was not worked by the Anaconda Company but apparently was the site of the earliest mining in the area.

The Gunsight mine, discovered in 1865 (Waring and Huguenin, 1919, p. 95), was most active from 1912-28. During this period, the mine yielded 55,000 tons of ore which averaged 7.84 percent lead and 9.38 ounces of silver per ton. Although the deposit was extensively explored to an inclined depth of nearly 1,000 feet, most of the ore came from a single shoot (Sampson, 1937, p. 267) that had a strike length of possibly 300 feet, a dip length of 600 feet and a maximum thickness of about 20 feet.

The Noonday mine, and the adjoining Grant mine to the south, likewise were active principally from 1912-28 and yielded about 93,000 tons of ore, most of which came from the Noonday and averaged 15.39 percent lead and 7.29 ounces of silver per ton. The average grade of the ore from the Grant was 11.05 percent lead and 8.87 ounces of silver per ton (Tucker and Sampson, 1938, p. 448). These deposits were explored for an aggregate strike length of nearly 2,000 feet and to an inclined depth of 600 feet.



Starting in 1947, when the Anaconda Company purchased the group of mines, the principal activity was at the Columbia and War Eagle. Extensive workings from adits and inclined shafts allowed exploration of the deposits to an inclined depth of 965 feet in the Columbia mine and 1200 feet in the War Eagle mine. An ore shoot in the War Eagle, continuous from the 500-level to the 690-level and possibly lower, yielded ore that contained 20 to 40 percent lead and about half an ounce of silver per ton for each percent of lead (Norman and Stewart, 1951, p. 80).

Prior to 1947, all the mines in the Shoshone group had yielded about 250,000 tons of ore that had a gross value of about \$5,000,000. More than half of this was produced by the Tecopa Consolidated Mining Company during the period 1912-28. Operations by the Anaconda Company resulted in the production of more than 160,000 tons of ore that contained about 40,000,000 pounds of lead, 6,000,000 pounds of zinc, 870,000 ounces of silver and 15,600 ounces of gold. One-third of this ore was of shipping grade, averaging 27 percent lead, 11 ounces of silver and 0.2 ounce of gold per ton (Carlisle, et al., 1954, p. 46). The operations were suspended late in 1952, but were resumed in 1956.

The Santa Rosa mine at the southern end of the Inyo Range also has been an important source of lead in California. Mining operations, which started in 1911, have yielded a total of 36,854 tons of ore containing 11,990,792 pounds of lead, 487,347 pounds of copper, 4,105 pounds of zinc, 426,543 ounces of silver and 478.7 ounces of gold (Mackevett, 1953, p. 4). The ore-bearing veins are in extensively silicated Permian (?) limestone exposed in windows of Tertiary and Quaternary (?) volcanic rocks. Most of the veins are north-trending and have formed along faults that lie parallel to the bedding; fissure filling was the dominant vein-forming process (Mackevett, 1953, p. 7). Oxidation has been extensive and nearly complete. The most extensive workings, which were driven on a single vein, extend to an inclined depth of 352 feet.

Several mines in the northern end of the Argus Range in Inyo County, principally in the Modoc district, have yielded appreciable quantities of lead ore. The Defense mine in the Modoc district is notable for the rare mineral coronadite ( $\text{MnPbMn}_6\text{O}_{14}$ ) which is abundant enough here to constitute an ore of lead and is associated with galena and its products of oxidation.

Most of the rest of the lead that has been mined in California has been a by-product of the copper and gold mines of the Sierran foothill and Klamath Mountains areas (see sections on copper and gold in this bulletin). Other areas that have yielded relatively small quantities of lead ore include the Clark Mountain district in northeastern San Bernardino County, the Santa Rosa district in Orange County, and the northern Panamint Range in Inyo County.

**Utilization.** Lead probably was one of the first metals to be won from its ores by smelting. The Chinese apparently used lead for coins as early as 2000 B.C., and some authorities claim the Egyptians used lead as early as 7000 to 5000 B.C. Roman artisans used lead extensively for water pipes and other articles. Lead pipes as large as 100 inches in diameter have been found in ruins

of ancient cities in Asia, Egypt and Greece (St. Joseph Lead Co., 1951, p. 31).

The properties of lead that make it most useful are its softness and workability, high specific gravity, extreme resistance to corrosion, and a combination of low melting point and high boiling point. It also forms many useful alloys and chemical compounds. The Lead Industries Association has estimated that, of the lead consumed in the United States, 10 percent is used primarily because of its specific gravity; 30 percent because of its softness, malleability and resistance to corrosion; 25 percent because of its alloying properties, and 33 percent because of the properties of its chemical compounds (Perry, 1945, pp. 66, 67).

About two-thirds of the lead used is in a metallic form, alone or alloyed. Although lead has a very wide variety of uses, about 84 percent is absorbed by five principal uses. In 1954, these were apportioned approximately as follows (Bishop and den Hartog, 1956, p. 6): storage batteries, 31 percent; tetraethyl lead gasoline, 15 percent; cable coverings, 12 percent; paint pigments, 10 percent; and construction (calking lead, solder, pipe, sheet, etc.), 16 percent.

The alloys of lead are broadly divisible into antimony alloys, bearing alloys, solders, type metals and low melting alloys. Lead is alloyed more frequently with antimony than with any other metal. The proportion of antimony in such alloys ranges from a mere trace to 25 percent. As this hardens the lead, so that it resists abrasion and mechanical damage, the alloy is used in cable covering, pipe and sheet lead, bearing metal, and grids for storage batteries. Lead-antimony-tin alloys are used in type metals. In such metals the addition of tin adds to the ease of casting at low temperature.

The low-melting eutectic alloys of lead with bismuth, tin, cadmium, or indium are unique in that the melting temperature of any one of these alloys is lower than the melting temperature of the individual components. In recent years, the use of this type of alloy in fire detection and alarm systems, in safety plugs for compressed gases and in many other types of equipment has expanded very rapidly. During World War II, the War Production Board placed these alloys under allocation to insure proper distribution to essential war industries.

The use of lead carbonate and oxides as pigments has increased slightly in recent years, but has not reflected the increased consumption of all pigments in the paint industry. Titanium oxide has been used increasingly as a substitute for basic lead carbonate as a white hiding pigment. The synthetic iron oxides are being used in place of litharge and red lead as hiding pigments. The largest single use of the oxides of lead is in storage battery manufacture. That industry uses nearly as much lead in the oxide form as in the form of antimonial lead.

Glass that contains lead has a higher refractive index than ordinary glass, thus leading to its use in decorative and household items such as fancy table glassware, in which brilliance is desired, and to its use in optical equipment. Optical glass may contain as much as 75 percent lead. Lead in glass also increases its electrical resistivity. Glass containing as much as 30 percent lead is used in the manufacture of television tubes and other electronic components.



Large amounts of lead are used to protect personnel from radiations, principally gamma rays, emitted in laboratories and atomic reactor installations. Efficient radiation protection is a function of density, and lead has the highest density of any commonly available material. Lead does not become radioactive after exposure to radiation and can be used continuously.

Substitutes for lead are increasing in number and quantity. Possibly the greatest competition lies in pigment manufacture, where titanium and zinc are the chief competitors, and in the cable covering industry, in which aluminum and extruded polyethylene are becoming more widely used. Lead continues to be essential, however, in the uses that consume the largest quantities, and new uses for lead continue to be found; for example, aluminum coated with vitreous enamel containing 30 to 50 percent lead has considerable potential as an exterior structural and ornamental material.

Lead is extremely resistant to corrosion, and a large proportion of lead in use can be recovered as scrap and made available for re-use. Lead has the highest recovery factor of the common metals. Recovery factors for lead have been estimated for several categories of use as follows (Merrill, 1951, p. 33): cable coverings, 90 percent; type metal, 90 percent; storage batteries, 85 percent; bearing metal, 60 percent; building metals (calking lead, sheet, pipes, etc.), 15 percent; and other non-destructive uses, 32 percent. The useful life of the product determines the recovery period for the lead contained therein. This may range from a few hours or months for type metal to possibly 20 years for cable coverings; recovery time for lead in storage batteries may be 2 to 3 years. On the basis of the recovery factors stated above, about 60 percent of the lead in use ultimately will be recovered as scrap. Lead is not recovered from such products as tetraethyl lead used in gasoline and pigments. The national production of reclaimed lead in 1954 was nearly 481,000 tons and for the seventh successive year surpassed the amount obtained from mines (Bishop and den Hartog, 1956, p. 5).

During 1954, all uses accounted for a domestic consumption of 1,094,871 short tons of lead. During the decade ending with 1954, the annual domestic consumption ranged from 956,000 tons in 1946 to 1,238,000 tons (an all-time high) in 1950; the average annual consumption for this period was 1,112,000 tons (Bishop and den Hartog, 1956, p. 6; Bishop and Mentch, 1956, p. 456).

Lead consumption in California during 1954 amounted to 67,260 tons, of which 60 percent was in the form of refined lead, 31.6 percent in the form of antimonial lead and the remaining 8.4 percent in other forms (Bishop and den Hartog, 1956, p. 7). Battery manufacturing is the largest lead-consuming manufacturing industry in California.

**Mining and Milling.** Lead ores in California are mined by normal underground methods, as contrasted with some of the very large-scale room-and-pillar methods used in mining the disseminated lead deposits of southeastern Missouri. At the Darwin mines, for example, most of the ore is mined in sub-level stopes.

All mines in California have yielded ore of shipping grade, and small operators have had to depend on shipping-grade ore. At the larger mines, however, the bulk

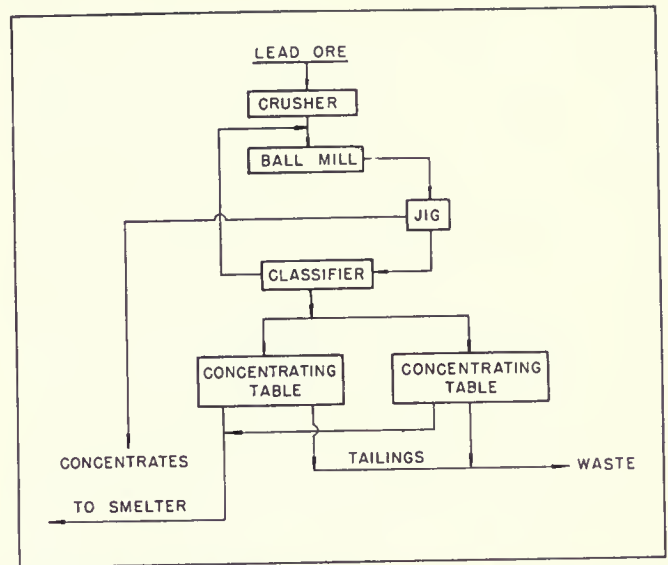


FIGURE 3. Schematic flowsheet of small gravity concentration plant. Adapted from description of Revard mill, Inyo County: Norman and Stewart, 1951, p. 49.

of the ore has been milled. At Darwin, for example, daily production of shipping-grade ore in 1953 amounted to only 25 tons, but daily mill capacity was 150 tons of oxide ore and 300 tons of sulfide ore (Carlisle et al., 1954, p. 44).

Lead sulfide minerals (and the zinc sulfide minerals in normal association) are readily amenable to concentration by the flotation process. Consequently, flotation is the most widely used method of concentration of lead ores. Gravity concentration, utilizing tables, jigs, or both, may be used in smaller mills (see fig. 3). If fine grinding is required to liberate the ore minerals from the gangue, excessive loss of values in the fines might decrease recovery below a profitable point in a straight

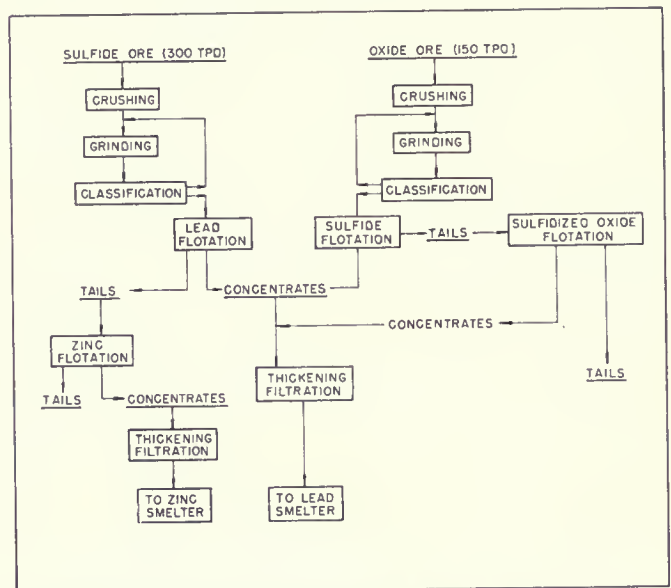


FIGURE 4. Schematic flowsheet of Darwin Mines mill. Adapted from Hutt, 1953, pp. 82-83, and Norman and Stewart, 1951, pp. 61-68.



gravity plant. Excessive loss usually is experienced in attempts to concentrate by gravity alone an ore in which much of the lead is contained in oxidized minerals, especially the brittle carbonate, cerussite. A more complex system is illustrated in the schematic diagram (fig. 4) of the mill at Darwin mines, in which both sulfide and oxide ores are concentrated.

In contrast to the sulfide ores, which are relatively easily concentrated by flotation, the oxidized ores first must be treated to effect sulfidization of the oxide minerals. This is accomplished by adding a water-soluble sulfide, usually sodium sulfide, to the circuit in the flotation cells after any intermixed natural sulfide minerals have been floated off. A surface reaction follows, and the oxide particles are coated with a very thin layer of lead sulfide. These surface-treated particles then can be floated as normal sulfide minerals. Cerussite is most amenable to this treatment, but anglesite reacts more slowly; treatment of other oxidized lead minerals, such as pyromorphite and wulfenite, has proved unsatisfactory (Gaudin, 1932, pp. 292-293). The grade of the oxide ore treated at Darwin averages 7 percent lead, and recovery is 87 percent (Huttl, 1953, p. 83).

*The Smelting Process—Selling Ores and Concentrates.* Lead is recovered from ore and concentrates by a smelting process that follows roasting or sintering of the ore to reduce the sulfur content. The roasted or sintered ore is charged, together with limestone and coke, into a blast furnace. The limestone and coke are necessary for slagging and reduction purposes. The lead is recovered as base bullion which may contain as much as 95 percent of the lead in the charge. The base bullion is treated at a lead refinery to produce refined lead and to recover precious metals (see section on silver in this bulletin). Figure 5 shows the flowsheet of the smelter of the

American Smelting and Refining Company at Selby in Contra Costa County.

The problems involved in smelting are reflected in the charges levied for processing the ore and in the payments made to the producer for the valuable metals contained in the ore. The payment for ore shipped to a smelter frequently is lower than the shipper had anticipated, and this often leads to disagreement between the shipper and the smelting company. Prospective shippers therefore should understand the factors involved in the determination of the net payments for material received at the smelter. The shipper should recognize that several charges are made for processing a shipment of ore, and that deductions of several types are made from the gross value of the ore.

Tables 1 and 2 summarize the charges and payments shown on the open schedules of three western smelters. A prospective shipper should contact a smelting company to obtain actual copies of open schedules, which are summary statements of the terms that may be used as a basis for the determination of payments for relatively small shipments. Shipments to which open schedule may be applied usually are limited to 100 to 200 tons per month. The open schedule is of service to a prospective shipper after he has had his ore assayed, in that it enables him to calculate the approximate net payment from the smelter. He should, however, send a representative sample to the smelter; after analyzing this sample, the smelting company will indicate the payment they will make for ore of the grade and type represented by the sample. Actual payment, however, will be based upon assays of samples taken from the shipment of ore after it has been received at the smelter.

Contracts that involve terms other than those stated in an open schedule commonly are drawn between the

Table 1. Smelter charges.\*

Charges for:	American Smelting, Refining and Mining Co. Selby, California	U. S. Smelting, Refining and Mining Co. Midvale, Utah	International Smelting and Refining Co. Tooele, Utah
Treatment charge-----	\$6.00 per ton	Base charges when dry assay is 30% lead: \$8.00 per ton Add 10 cents per ton for each unit of lead under 30% Credit 10 cents per ton for each unit of lead over 30%	\$8.50 per ton
Insoluble (silica)-----	10 cents per unit		
Arsenic, antimony and tin combined	1% free; excess charged at 50 cents per unit	Arsenic: charge for all at \$1.75 per unit	Arsenic and antimony: charge for all at 50 cents per unit
Zinc-----	7% free	6% free	Charge 15 cents per unit if zinc is paid for; if no payment for zinc, 6% free, and excess charged at 25 cents per unit
	Charge for excess at 30 cents per unit		
Bismuth-----	Charge for all at 50 cents per pound	Shipment subject to rejection if more than 0.1%	Probable charge but not stated
Sulfur-----	Maximum charge \$2.50 per ton	2% free. Excess charged at 25 cents per unit Maximum charge \$3.00 per ton	Maximum charge \$2.50 per ton
Moisture-----	1% deduction on wet weight of shipment. Actual moisture weight deducted up to content of 10%. Charge 10 cents per unit for excess of 10%.	Not stated, but deductions made	

\* Information summarized from open smelter schedules.



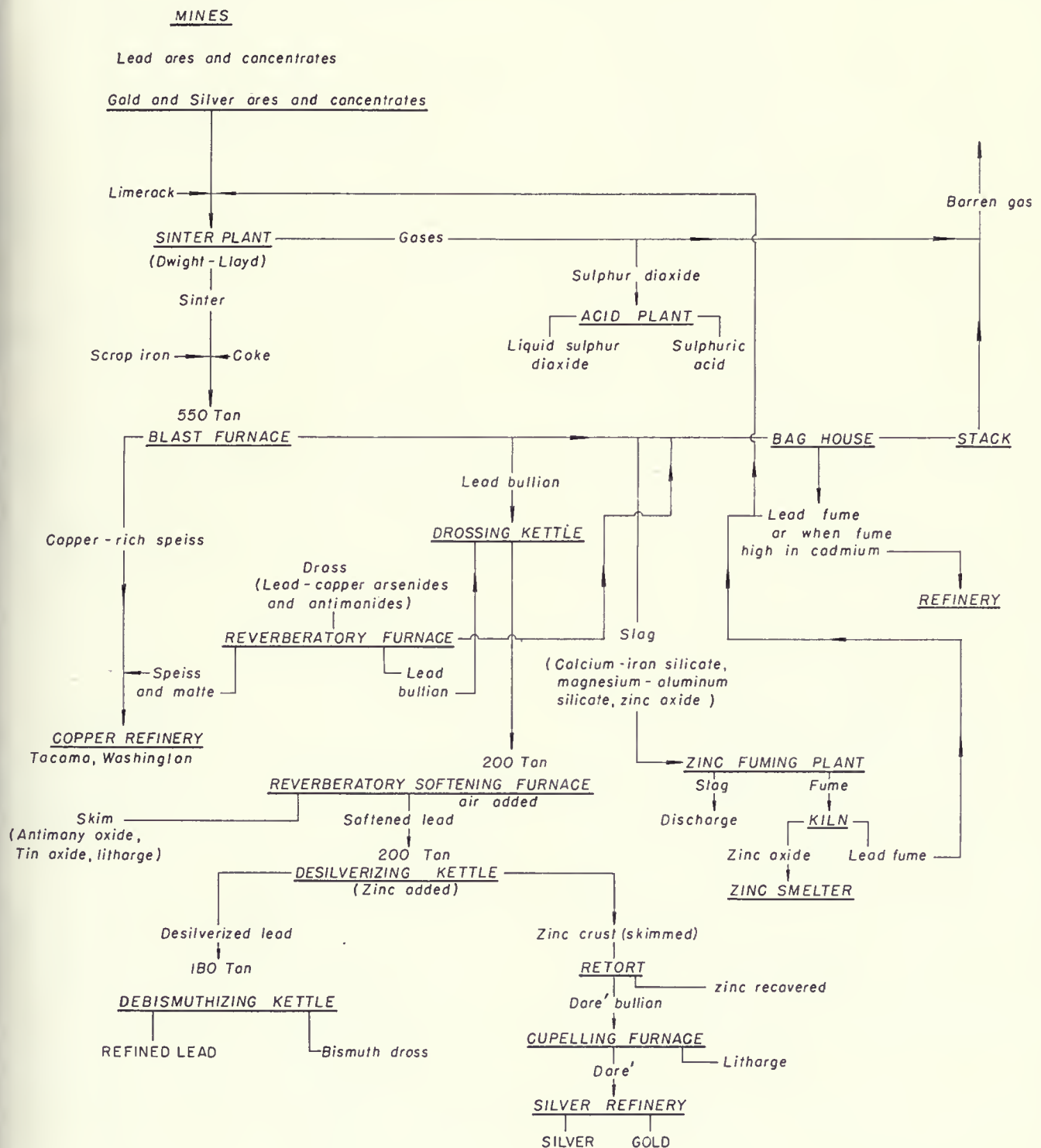


FIGURE 5. Flowsheet, Selby lead smelter, American Smelting and Refining Company. Adopted from Davis, 1951, p. 595.



Table 2. *Smelter payments.\**

Payment for:	American Smelting, Refining and Mining Co. Selby, California	U. S. Smelting, Refining and Mining Co. Midvale, Utah	International Smelting and Refining Co. Tooele, Utah
Lead.....	No payment if lead below 3%. Deduct 1½ units from wet assay; pay for 90% of remainder at market** price less: 2.00 cents per pound	2.3 cents per pound	2.2735 cents per pound
Gold.....	Pay for 91.14% of all over 0.03 oz. per ton at net Mint price	0.02- 0.5 oz.   \$31.8183 per oz. 5.0 -10.0 oz.   \$32.3183 per oz. over 10.0 oz.   \$32.8183 per oz.	Pay for 91% of all over 0.02 oz. per ton at net Mint price
Silver.....	Minimum deduction 1 oz. per dry ton	Minimum deductions of ½ oz. per dry ton No payment if less than 1 oz. per ton	Pay for 95% at market price
Copper.....	Deduct 1.3 units from wet assay. Pay for rest at market price less 8 cents per pound. No payment if less than 1.3%.	Pay for 90% of wet assay. (Minimum deduction 15 pounds) at market price less 8.5 cents per pound	Deduct 15 pounds per ton. Pay for rest at market price less 7.6235 cents per pound
Iron.....	Pay for all at 6 cents per pound		
Lime.....	Pay 5 cents per unit for all over 5%		
Zinc.....	If over 10% pay for 75% at 22% of East St. Louis price for Prime Western quality		

\* Information summarized from open smelter schedules.

\*\* Market price is quotation as of delivery date or average of prices for a period as specified in contract or schedule.

smelting company and individual producers. A shipper who can make large regular shipments or provide an ore with especially desirable constituents may receive terms that could involve lower treatment charges or premium payments for some of the constituents of the ore.

The many factors shown in open schedules can be grouped into three principal headings: (1) treatment charges, (2) penalties, and (3) payments.

The basic treatment charge covers the costs of smelting and must include (1) the actual costs of labor, fuel and supplies; (2) funds to cover interest, obsolescence and depreciation on plant and equipment, and insurance; (3) costs of supervision, management, office and selling; and (4) profit (Tyler, 1945, p. 259).

Penalties are charged for constituents of the ore that require special consideration in formulating a furnace charge or for impurities that enter into the base bullion and require extra treatment processes for their removal.

The reactions in the blast furnace effect the reduction of lead compounds to metallic lead and the formation of matte and slag of such composition and physical characteristics that a clean separation of all can be made. Bowman (1945, p. 160) states that, "The specific gravity of liquid (molten) lead is about 10.5, that of matte ordinarily ranges from 4.5 to 5. In order to ensure a satisfactory separation of matte and slag, the specific gravity of the latter should be at least 1.0 lower than the lightest matte." Also, the slag should be fusible at 1100 to 1200° C., should have a specific gravity no higher than 3.6, and should be of a satisfactory chemical composition.

Slag is a complex silicate, and its melting point and specific gravity are determined by the silica:lime:iron ratio. Most ores are not self-fluxing, that is they do not contain all the materials necessary to allow the clean separation of metal, slag and matte as outlined above. Ingredients must be added to the furnace charge to maintain a proper metallurgical balance. A highly siliceous ore requires additions of iron and lime, and an ore that is too calcareous or ferruginous must have silica added. Manganese sometimes is considered the equivalent of

iron as a flux for silica, and magnesia, zinc oxide or barium oxide may be substituted for lime (Bowman, 1945, p. 162). Fluxes add to the cost of the charge, so penalties are levied for constituents of the ore that require fluxing. If a smelter is processing a siliceous ore that requires iron or lime for fluxing, silica is penalized and payments are made for iron and lime. The addition of fluxes also decreases the proportion of the ore in the charge, thus increasing the cost per unit of valuable metal recovered. In current lead smelting practice, the ore usually constitutes 80 percent or more of the charge (Bowman, 1945, p. 162).

The effects of some of the common constituents and impurities for which penalties are exacted as shown in table 3.

Payments are not made for the full amount of metals that assays indicate are present in the ore, nor are they made at the full market price for the metals. Deductions from the gross lead content are calculated to compensate for losses in treatment, and payment is made for the remainder.

Smelting efficiency is high. Bowman (1945, p. 164) states that blast-furnace smelting should yield 95 to 98 percent of the lead in the charge; Bishop and Mentch (1956, p. 430) state that primary lead smelters generally recover 97 to 98 percent of the lead in the charge.

As shown in table 2 a lead-smelting company will pay for silver, gold, copper, iron, and in some instances, zinc, in addition to the lead that is contained in the ore. The payment for iron is at a fixed rate and for gold is determined by the Mint price; payment for all other metals is calculated on the basis of a market price quoted on a given date or that represents a weekly average. Methods for determining the applicable market prices are not uniform, and are as follows: (1) lead—average price for calendar week including or preceding the date of delivery of ore to the smelter; (2) silver—the Mint price, or the Handy and Harman New York price as of the date of delivery, or the average price for the calendar week including or following the date of delivery; (3) copper—average price for the calendar week pre-





FIGURE 6. Lead deposits in Inyo County. Adapted from Norman and Stewart, 1951, pl. 1

ceding or including the date of delivery; (4) zinc—average price for week ending Wednesday preceding date of delivery. Prices quoted in the Metal and Mineral Markets (a weekly publication) are accepted as standard.

The smelter of the American Smelting and Refining Company at Selby in Contra Costa County is the only primary lead smelter in California. The published capac-

ity of the plant is 192,000 tons of charge per year; the lead refinery, operated in connection with the smelter, has an annual capacity of 72,000 tons of refined lead (American Bureau of Metal Statistics, 1956, p. 46). Actual production annually of refined lead is lower, however, and currently averages about 60,000 tons, about one-half of which is shipped to consumers in California, Oregon, and Washington (Playter, G. H., 1956, personal

Table 3. Effects of impurities on smelting process.

Silica.....	Requires additional iron or lime to make a desirable slag.
Arsenic, antimony and tin (0 to 1% free).....	Sometimes grouped together; combined content subject to penalty. Effects discussed individually below.
Arsenic.....	Contaminates the flue dust collected from blast furnace. Arsenic forms speiss, a basic arsenide of iron, which has a great affinity for gold and must be separately treated to recover gold. Some arsenic as well as antimony and tin also contained in base bullion. (See next item.)
Antimony and tin.....	Makes the lead hard and necessitates treatment of the base bullion in a softening furnace.
Zinc (6 to 7% free).....	Tends to make a thick viscous slag that increases metal loss and lowers furnace capacity. As zinc volatilizes, it increases the loss of other metals, especially silver, and fouls the furnace walls.
Bismuth.....	Not removed in ordinary refining processes and may be carried into refined lead. Hardens lead and discolors white lead pigments. "Corroding lead", containing less than 0.05 percent bismuth, must be used for pigment manufacture. Excessive bismuth may be a cause for non-acceptance of an ore for smelting.
Sulfur (2% free).....	Forms excessive matte. Sulfur content must be decreased by roasting or sintering before ore is charged into blast furnace; this treatment increases smelting cost.
Moisture.....	Ore must be converted to dry basis for weight calculations, so weight of moisture is deducted. Normally a deduction of one percent is made, whether ore is dry or not, to cover dusting losses. If moisture is more than 10 percent, the ore might hang up in bins or otherwise add to handling costs.





FIGURE 7.



communication). The smelter subsists largely on ore imported from sources in South America—Peru, Bolivia, and Chile in that order—and from Australia.

All of the concentrates and shipping-grade lead ore produced in California by the Anaconda Copper Mining Company are shipped to the Tooele, Utah, smelter of the International Smelting and Refining Company, a wholly controlled subsidiary of the Anaconda Company. Other producers choose between the smelter at Selby, California and other smelters in the western states. Freight rates bear importantly on such a choice.

Freight rates for ores of most metals, lead included, are dependent not only on the points of origin and destination, but also upon the value of the ore and the amount shipped. The higher the value of the ore, the greater is the rate per ton. Also, the rate is greater for shipping 20 tons than for shipping 50 tons. In preparing a waybill, the initial document covering a shipment, the ore is presumed to be worth \$100 per ton and charges made accordingly. When a settlement is made at the smelter, the lead content of the ore is certified to the railway, and the value of the ore is determined using an arbitrary value for lead of 7 cents per pound. The correct freight charge per ton of ore is determined and the amount charged on the initial waybill revised upward or downward. Examples of freight charges that were effective early in 1957 for lead ore are shown below (Southern Pacific Company, personal communication).

For shipping ore from Lone Pine or Olancho, California:

To	Minimum weight	Dollar value per ton	Cost per ton, dollars
Tooele, Utah -----	50 tons	60	12.53
Tooele, Utah -----	50 tons	20	9.53
Selby, California -----	50 tons	60	9.96
Selby, California -----	20 tons	60	11.35

Freight charges are subject to published and negotiated changes.

Efforts to treat lead ore in portable smelters or small smelters at ore near the mines in California have not been successful. Liddell (1945, p. 580) states, concerning the general aspects of the problem, "Thirty to forty years ago it was customary to consider the equipping of small base-metal mines with small smelters to make them independent of the so-called 'Smelter Trust,' and to save long hauls on ores. That plan proved infeasible, and the day of small smelting plants built in narrow out-of-the-way canyons has probably passed. To make a profitable smelting enterprise, a large tonnage of ore must be available, together with the necessary flux which requires either a very large mine or a district producing a diversity of ores that will provide a suitable smelting mixture."

**Marketing Refined Lead.** The marketing of lead ores and concentrates discussed in the preceding section, is the first of two separate but interrelated types of marketing operations that exist in the lead industry. The sale of refined lead and alloys of lead is the second type. The principal sellers of refined lead in the United States are the American Smelting and Refining Company and the St. Joseph Lead Company. These two companies market 50 to 75 percent of all refined primary lead, the propor-

tions being modified by the quantities of lead being imported (Bishop and Mentch, 1956, p. 427).

A simplified classification of refined primary lead has been adopted by the American Society for Testing Materials, and only four grades of pig lead are generally marketed domestically in contrast to seven grades recognized prior to 1955. These four grades may be described briefly as follows (American Society for Testing Materials, 1956, pp. 71-74; Bishop and Mentch, 1956, p. 427):

Corroding lead—a premium-grade, high-purity lead made by re-refining desilverized or chemical lead.

Chemical lead—a premium-grade, undesilverized lead produced from southeastern Missouri ores. These ores contain too little silver for profitable desilverization.

Acid-copper lead—a premium-grade lead made by adding copper to fully refined, desilverized lead.

Common desilverized lead—fully refined, desilverized lead made from argentiferous lead ore.

Most of the lead marketed domestically is sold at a price based upon the published quotations for lead in either the New York or St. Louis markets. American Smelting and Refining Company prices are based upon the New York quotations, and the St. Joseph Lead Company prices are quoted on the St. Louis market (U.S. Bur. Mines, 1951, ch. 6, p. 31). The New York prices are about 0.2 cents per pound higher than those at St. Louis, this difference approximating the freight charges between the two points. The annual average New York prices for lead are plotted on figure 1.

The prices for alloys of lead and for other lead-containing materials bear a fixed relationship to the price of pig lead.

**Government Programs.** The government has regulated the lead industry during emergencies, such as World War II, in an effort to provide adequate supplies of lead for all essential uses. The regulations placed in effect consisted of controls over prices, imports and exports, priorities and allocations, and inventories. In addition, various programs were undertaken to stimulate production of lead from domestic sources.

One of these programs, the Premium Price Plan (Olund and Gustavson, 1950, 210 pp.) involved the payment of a premium price for lead (as well as for copper and zinc) produced in excess of a quota based upon 1941 output. A quota for a mine or group of mines and the amount of premium to be paid were determined according to involved and complex regulations. During the life of this plan (February 1942 to June 1947) 45 percent of all domestically mined lead brought premium prices. The weighted average price for lead paid during this period was 8.84 cents per pound; this included an average premium of 2.61 cents per pound (Bishop and Mentch, 1956, p. 25).

Other government activities during World War II included stockpiling by the Metals Reserve Company and exploration-development programs by the U. S. Geological Survey and U. S. Bureau of Mines.

The Defense Act of 1950, inspired by the critical developments of the war in Korea, established several organizations to assist the mineral industry. One of these, the Defense Minerals Exploration Agency, will make loans amounting to 50 percent of the cost of ap-



proved projects that are intended to explore deposits of lead ore.

Since the termination of the Korean war, the policies for determining stockpile objectives have been re-examined in the recognition of a greater need for supply protection during wartime. In 1954, a long-term stockpile program for metals and minerals was announced by the President. This program sets long-term objectives to be met in part by the purchase of metals and minerals to assist in maintaining the domestic production component of the nation's mobilization base. Long-term objectives for lead were included, and purchases of newly mined lead from domestic sources were started in June 1954.

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## LIMESTONE, DOLOMITE, AND LIME PRODUCTS

By OLIVER E. BOWEN, JR.

California's extensive deposits of limestone, sea shells, magnesian limestone and dolomite have all played important parts in the rapid industrial development of the state. They are basic resources upon which such essential enterprises as the portland cement, lime, calcium chemical, sugar refining and magnesia refractories industries are directly dependent. The portland cement industry alone consumed more than 9,000,000 tons of limestone and sea shells in 1955, producing finished products worth more than \$103,300,000 at the mill. A surprisingly large number of other industries are directly or indirectly dependent upon carbonate raw materials. Consumption of carbonate materials is constantly increasing.

### COMPOSITION AND PROPERTIES OF LIMESTONE, DOLOMITE, AND OTHER LIME-BEARING MATERIALS

Limestone, magnesian limestone, dolomite, magnesite and sea shells are the chief natural sources of calcium and magnesium carbonates in California. Inasmuch as California magnesite has a different origin, geologic occurrence and usage than other calcium and magnesium carbonate rocks, it is not included in this summary and is discussed separately in the bulletin.

As calcium and magnesium are easily interchanged in the atomic structure of carbonate minerals, there are numerous transitions between the minerals calcite ( $\text{CaCO}_3$ ), dolomite ( $\text{CaCO}_3 \cdot \text{MgCO}_3$ ) and magnesite ( $\text{MgCO}_3$ ). Sea shells are secreted wholly, or in a few cases partly, as the mineral aragonite ( $\text{CaCO}_3$ ) by the living organisms and with time generally recrystallize entirely to calcite (also  $\text{CaCO}_3$ ). Sea shells of most marine animals contain only small proportions of magnesium, although the shells of some species contain up to 12 percent magnesium oxide (Chave, 1954, pp. 261-273; 1952, pp. 190-192; Clark and Wheeler, 1917). When present the magnesium generally occurs replacing calcium atoms in the normal calcite structure and is not present as the mineral dolomite.

Rocks composed predominantly of the mineral calcite are called limestone; those in which the mineral dolomite predominates are called rock dolomite or simply dolomite. Pure limestone, which is rare, contains 100 percent  $\text{CaCO}_3$ . Rocks composed of mixtures of calcite and dolomite or rocks composed of carbonate minerals transitional between calcite and dolomite are called magnesian limestones. In general, limestones, dolomites and magnesian limestones cannot be used interchangeably and economic utility of these rocks must be judged by their chemical and, for some uses, physical characteristics. Most commercial limestone contains more than 95 percent  $\text{CaCO}_3$  and less than 5 percent  $\text{MgO}$ , although rock of lower  $\text{CaCO}_3$  content is sometimes used—particularly for portland cement. Limestone containing more than 95 percent  $\text{CaCO}_3$  is commonly referred to as high-calcium limestone. Magnesian limestone is commonly designated as rock having from 5 to 15 percent  $\text{MgO}$  and rock dolomite from 15 to 21 percent. Dolomite rocks containing more than 21 percent  $\text{MgO}$  would normally contain some magnesite; such rocks are rare in California.

Marl is a clayey and therefore aluminous and siliceous variety of carbonate rock that most commonly is earthy or friable. Some marl is a caliche type of material formed by evaporation of carbonate-laden groundwater in soil. Marl also forms as a clayey marine or freshwater deposit. The most common carbonate constituent is calcium carbonate, but magnesian marls are known to exist.

All of the rocks composed predominantly of carbonate minerals are convertible into metallic oxides and carbon dioxide gas ( $\text{CO}_2$ ) if heated beyond the critical temperature of dissociation for the constituent minerals. The dissociation temperature range for calcite or pure limestone is  $725^\circ \text{C}$ . to  $1000^\circ \text{C}$ .; other carbonate minerals decompose at temperatures ranging from  $545^\circ \text{C}$ . to  $1500^\circ \text{C}$ . Lime ( $\text{CaO}$  or quicklime) is the solid dissociation product derived by calcining (burning) limestone; magnesian lime (a mixture of  $\text{CaO}$  and  $\text{MgO}$ ) is derived from magnesian limestone or dolomite; and magnesia ( $\text{MgO}$ ) is derived from magnesite. The metallic oxides combine readily with water with evolution of heat to produce hydrated lime ( $\text{Ca(OH)}_2$ ) and magnesia ( $\text{Mg(OH)}_2$ ) or mixtures of these hydrates.

Although metallic magnesium has been produced in California for short wartime periods the present economic importance of the carbonate rocks lies in either the metallic oxide or carbon dioxide content, neither of which have a metallic aspect. Consequently, the common carbonate rocks are generally classified as non-metallic minerals.

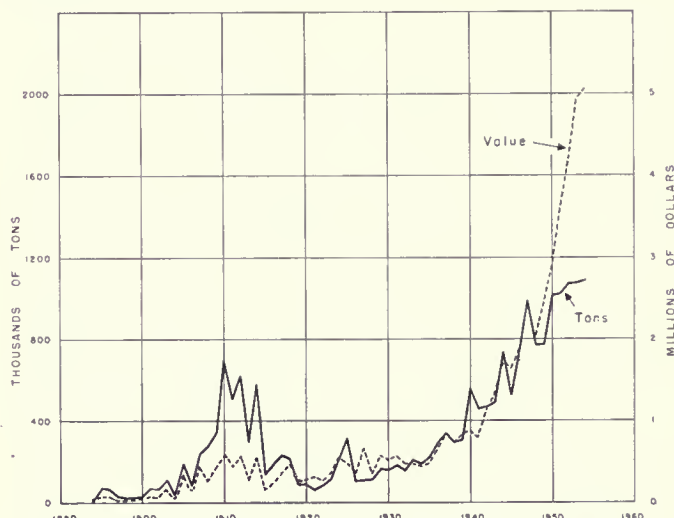


FIGURE 1. Graph showing amount and value of limestone and dolomite produced in California between 1894 and 1955. The graph is not a precise index of amount and value over this period because there have been several changes in the manner of reporting limestone and dolomite statistics over the years. For example, the figures on dolomite were tabulated separately between 1915 and 1946, these additional figures being available on page 70 of Division of Mines Bulletin 139, *Mineral Production in California in 1946*. Also, limestone and dolomite utilized simply as crushed or broken stone have been included in the summary some years and not others. In recent years, dolomite production statistics have not been listed separately in order to keep confidential the business of the small number of California producers. The limestone utilized in lime manufacture is not included in the graph.



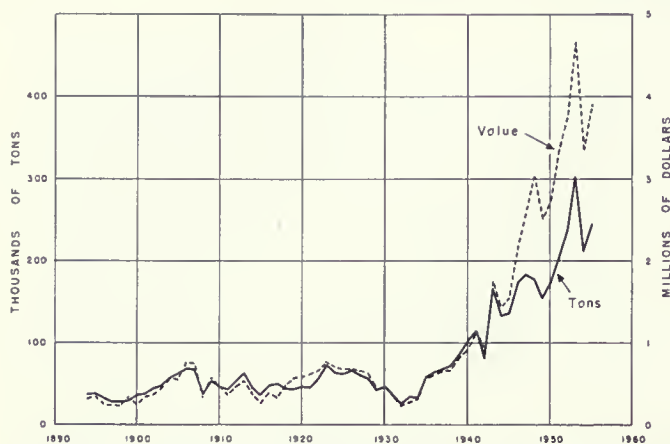


FIGURE 2. Graph showing amount and value of lime produced in California 1894-1955. Included in the graph are magnesian lime and calcined dolomite, which cannot be listed separately because of the small number of producers. The amount of limestone and dolomite consumed in the manufacture of lime products can be calculated roughly by taking the lime tonnage as 56 percent of the total limestone used (approximately 44 percent of the limestone is driven off as carbon dioxide). The yield of lime from magnesian limestone and dolomite is slightly smaller than from high-calcium limestone.

#### ORIGIN AND MODE OF ACCUMULATION OF LIME-BEARING MATERIALS

Many aquatic organisms, both plant and animal, secrete calcium carbonate for protective and supporting parts. As many of these organisms are colonial or at least gregarious in habit, their limy remains may accumulate and be preserved in large concentrations. Micro-organisms may also contribute indirectly to the chemical precipitation of carbonate minerals by upsetting the chemical equilibrium of the aqueous system, by catalytic activity and so on. Changes of temperature and changes in mineral concentration and composition of ocean and lake waters may also result in precipitation of carbonate minerals without the aid of organisms. The relative importance of purely chemical precipitation as compared with the action or influence of organisms in producing limestone has not been well established, but organisms appear to play the predominating role in limestone formation, and mechanical concentration of pre-existing carbonate detritus as well as inorganic chemical precipitation play lesser roles. Nevertheless, some California limestone formations consist predominantly of debris eroded from pre-existing carbonate rocks, and many great thicknesses of recrystallized carbonate rocks may well have lost their original detrital character during metamorphism. Consequently, the detrital mode of accumulation has been significant in California.

A few deposits of limestone, which are of sufficient size and purity to be of economic importance, have formed by a combination of evaporation and chemical interaction between carbonate-laden spring water and air. Such material, which is known as travertine limestone, grows by accretion around multiple spring vents and occasionally builds deposits aggregating tens of millions of tons. Algae, bacteria and other organisms may aid the process.

Some sea-floor carbonate deposits also grow by accretion of tiny, interbonded mineral crystals, but the bulk

of most marine- and lacustrine-laid limestones are believed to originate as soft, unconsolidated oozes which are compacted and finally lithified long after burial under succeeding strata. Consolidation and lithification of soft oozes generally involves widespread re-solution, cementation, dehydration and crystallization, the ultimate rock having few voids and consisting principally of interlocking crystals. Microscopic examination of some limestones shows that some material forms by dehydration of colloidal carbonate gels without crystallization in early stages of lithification. However, colloidal material probably does not form the major parts of most limestone deposits.

Limestones also accumulate by direct growth of reef-building organisms such as corals or the lime-secreting algae *Lithothamnion*. Reef limestones differ from accumulations of sea shells in that most of the shell deposits have been transported to some extent by water, whereas the bulk of reef limestone generally is secreted in place by colonial organisms.

The spectacular calcareous tufa deposits seen along the present and ancient shore lines of desiccating saline lakes in California and Nevada most commonly form by action of lime-secreting algae. Many algal tufa deposits grow in much the same fashion as coral reefs, but the resulting deposit is relatively structureless as compared to the normally well preserved colonial corals. Calcareous tufa deposits are generally too small to be of economic importance, although a few travertine deposits are large enough.

Calcareous deposits of considerable size also form in desert climates as the result of evaporation of carbonate-laden groundwater. These calcareous evaporites or caliches, as they are commonly called, may form at or close to the surface or they may form deeper in the pervious mantle above locally-developed impervious layers. Caliche was the principal raw material used at the early-day Jamul Ranch cement plant in San Diego County and is used to some extent today at several of the desert cement plants.

Dolomite may originate as a chemical or biochemical precipitate in much the same ways as those discussed for limestone, but such dolomite masses are generally small. More commonly dolomite is derived by chemical replacement of limestone. Such replacements may take place upon the sea floor during accumulation of the sediment, or much later—in many cases long after consolidation, lithification and elevation of the sediment above sea level have taken place. Dolomitization, the process of forming dolomite by chemical replacement, is a phenomenon that commonly accompanies hydrothermal alteration and ore-mineral deposition. There is considerable evidence that dolomitization is associated with the intrusion of granitic rocks, particularly where there has been large-scale invasion of granitic rock. However, the most important environment in dolomitization is believed to be ocean-floor replacement brought about by small changes in the physico-chemical environment over long periods of sedimentation.

#### OCCURRENCES OF LIMESTONE AND DOLOMITE IN CALIFORNIA

Most of the limestone and dolomite deposits in California occur in metamorphosed marine sedimentary rocks



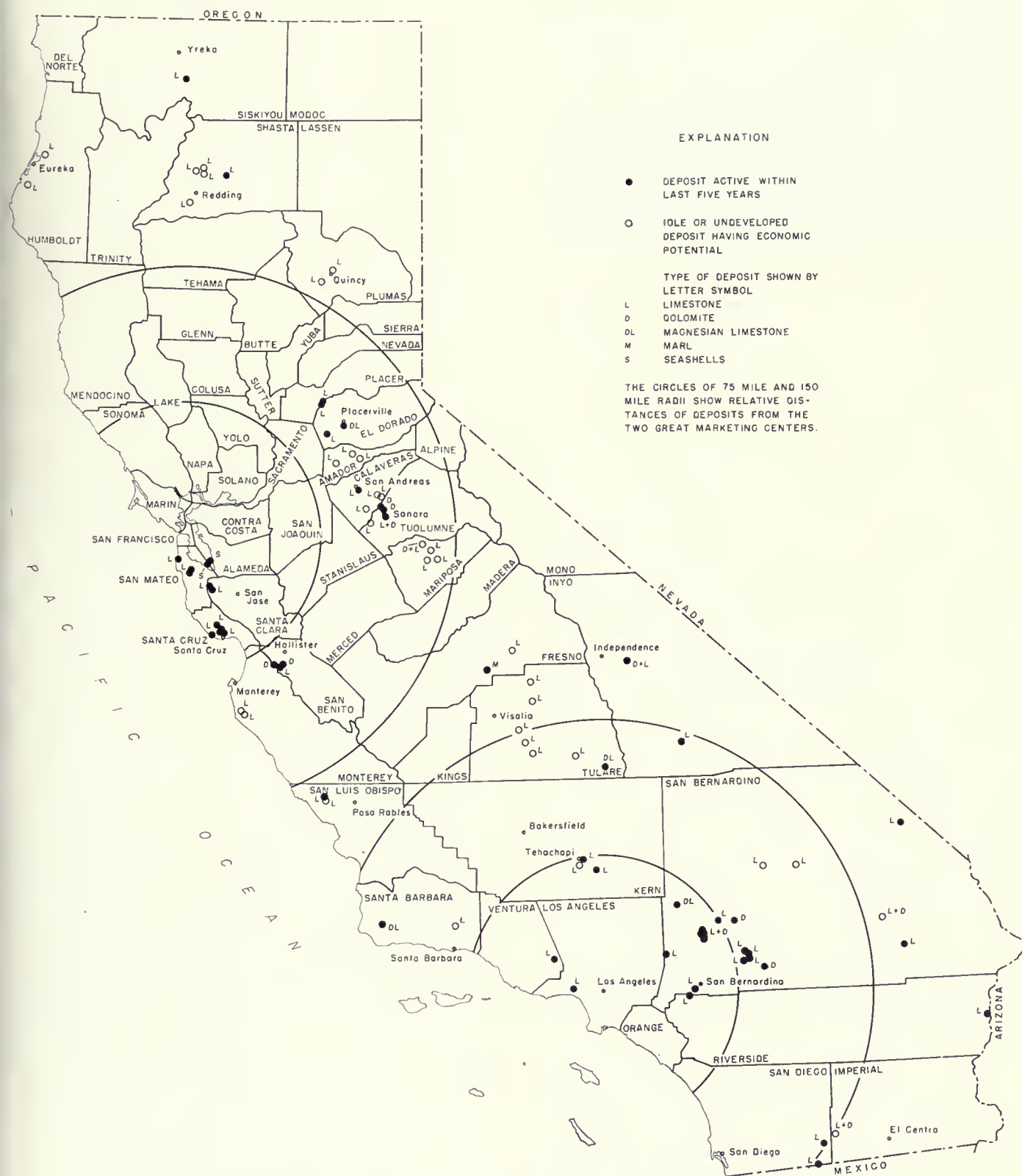


FIGURE 3. Map showing distribution of the active deposits of limestone and dolomite in California.





FIGURE 4. Southwestern Portland Cement Company's Black Mountain limestone deposit in the Sidewinder Mountains 14 miles east of Victorville, San Bernardino County. The entire mountain above the blasting strip is limestone conglomerate of Permian age. Since the photograph was taken, about 1952, almost all of the triangular hill in the middle ground has been quarried for use in cement. Total reserves of limestone in this deposit, above local base level, amount to more than 300 million tons. *Photo courtesy Southwestern Portland Cement Company.*

that have been strongly deformed. Most commonly they are found in rocks of Paleozoic age, but there are some commercial deposits in rocks of Mesozoic age and a few are found in pre-Cambrian suites of rocks. There are deposits of Tertiary algal limestone of good grade in the Sierra Blanca formation of Santa Barbara and Ventura Counties and Miocene shell limestone is extensively quarried at Lime Mountain in San Luis Obispo County for use in sugar refining. Travertine (warm-spring) limestone of Recent age has been utilized in the San Francisco Bay area and Quaternary accumulations of sea shells have been exploited at San Francisco, Newport and San Diego Bays. Marl has been quarried in a small way from pits in the Minkler district of Fresno County but deposits are not very extensive and demand has been small. Chalk, or earthy foraminiferal limestone is not found in California.

The principal areas where carbonate rocks are abundant and reasonably near to markets and to transportation facilities are: (1) the Klamath Mountains of Shasta and Siskiyou Counties; (2) the foothill belt of the Sierra Nevada from Placer to Tulare County; (3) the Santa Cruz, Gabilan, and Santa Lucia Mountains of the central Coast Ranges; (4) the Tehachapi Mountains within the Mojave-Monolith-Frazier Mountain triangle; (5) the Victorville-Oro Grande-Adelanto region of the southwestern Mojave Desert; (6) the north slope of the San Bernardino Mountains adjacent to Lucerne Valley; and (7) the northern part of the San Jacinto Mountains, including the Palm Springs-Lake Hemet and Beaumont-San Jacinto areas.

Four formations yield commercial limestone in Shasta and Siskiyou Counties: the Hosselkus limestone (Triassic), the Kennett limestone (Devonian), the McCloud limestone (Permian) and the Silurian limestone near Gazelle, Siskiyou County. The first three formations extend south into northern Plumas County but are not recognized elsewhere in the Sierra Nevada. Commercial limestones from these formations range from light dove-gray to black and generally are dense, fine-grained, weakly metamorphosed rocks. Of the four formations the McCloud limestone probably contains the largest re-

serves, but in the most accessible parts exposed south of Shasta Dam Lake both magnesia and silica tend to be sporadically distributed in the limestone. The Hosselkus formation contains the most uniform commercial-grade rock of any of the four formations sampled by the Division of Mines. Dolomite is known to occur in the McCloud limestone, but commercial deposits have not been developed thus far. Limestone has been quarried at Gazelle, Siskiyou County, and Ingot, Shasta County.

In the foothill belt of the central Sierra Nevada commercial limestone and dolomite deposits are found in a discontinuous series of simple lenticular masses enveloped in other metamorphic rocks or in granitic rock; they also occur in masses having complicated outlines because of intense folding. A few of the limestone bodies have yielded fossils ranging from Permian to Mississippian age, but fossil evidence is very sparsely distributed. Carbonate rocks of Mesozoic age have not been recognized in the central foothill belt. The principal districts producing commercial limestone are: Cool-Cave Valley, El Dorado County; San Andreas, Calaveras County; and the Sonora-Columbia area, Tuolumne County; and Diamond Springs, El Dorado County.

The crystalline limestones of the central part of foothill belt are associated with metamorphosed sedimentary and volcanic rocks of the Calaveras group, principally slate, mica schist and greenstone. The largest masses of limestone are found east of the Mother Lode, but these commonly are medium to coarsely crystalline. A succession of relatively small lenses (none more than a quarter of a mile long or more than 300 feet thick), of dense, fine-grained, blue-gray or dove-colored limestone is found in a narrow belt in the extreme western foothill area from Placer County south to western Calaveras County. These limestone lenses have been much less intensely metamorphosed than those east of the Mother Lode and limestone taken from them holds its lump form much better during calcination. The chemical composition of the rocks also is more uniform than in most of the more easterly deposits. Consequently, limestone from this belt is commonly superior to rock from other central Sierran deposits for some uses.

Limestones of the Sierran foothills most commonly are blue-gray, and white. Dolomite generally is white or off-white and almost invariably occurs as irregular replacements in limestone. Many of the limestone masses are too magnesian to be useful for purposes other than manufacture of magnesian lime, although there are a few nearly pure calcitic and dolomitic masses scattered throughout the foothill area from which commercial rock is obtained without selective mining. The Sonora-Columbia district contains the largest continuous masses of carbonate rock in the Sierra Nevada, some covering dozens of square miles. In this district, however, the presence of numerous patches of replacement dolomite of very irregular shape makes selection of quarry sites difficult.

Granitic intrusions and complex fold structures complicate mining and quarrying of carbonate rocks in many parts of the Sierra Nevada. South of Fresno County faulting along the western border of the mountains has raised the granitic core and resulted in stripping of the carbonate-bearing pendants by erosion to a far greater extent than in the central and northern Sierra Nevada.



Consequently, limestone and dolomite deposits are much more sparsely and haphazardly distributed in the southern Sierra Nevada than elsewhere along the Sierran foothills.

Carbonate-rock deposits of notable size and favorable geographic position in the western Sierra Nevada are concentrated in the Worth district, east of Porterville; in the Three Rivers district northeast of Visalia; in the Briceburg district of Mariposa County; the Sonora-Columbia district of Tuolumne County; the Copperopolis and Valleeitos districts of Calaveras County; and the foothill gold belt from Jackson to Auburn in Amador, El Dorado and Placer Counties.

In the central Coast Ranges large roof-pendants of crystalline limestone and dolomite are found in ancient, probably Paleozoic complexes in the Santa Cruz, Gabilan and Santa Lucia Mountains and in the Sierra de Salinas. Carbonate rocks of these complexes commonly are coarse-grained, and white and blue-gray colors predominate. Both high-grade limestone and high-grade dolomite occur in deposits large enough for major exploitation (masses aggregating tens to hundreds of millions of tons), deposits of the northern Gabilan Range and southern Santa Cruz Range supplying much of the current demand in the San Francisco Bay area. Nearly all of the dolomite currently used in northern California is quarried from deposits in the northern Gabilan Range. Dense, fine-grained limestones found in the Franciscan group of sediments of Jura-Cretaceous age also supply notable tonnages to San Francisco Bay industries, particularly to the cement plant at Permanente, Santa Clara County. Quaternary oyster shells dredged from San Francisco Bay supply one cement plant at Redwood City, San Mateo County.

Tertiary unmetamorphosed limestones of considerable present economic importance and even greater future significance as the population increases, are sparsely distributed in the southern Coast Ranges of San Luis Obispo, Santa Barbara and Ventura Counties. Beds of shell limestone of the lower Miocene Vaqueros formation are quarried at Lime Mountain west of San Miguel for use in sugar refineries of Salinas Valley. Deposits of algal limestone in the Eocene Sierra Blanca formation can supply good quality, dense limestone to industries in Santa Barbara and Ventura Counties should the demand arise.

Broad expanses of carbonate rocks lie in the Tehachapi Mountains in the triangular area bounded by Frazier Mountain, Mojave and Monolith. Occurring as pendants encased in granitic rock, the carbonate rocks may be found alone or interbedded with mica schist and quartzite in the Bean Canyon series of late Paleozoic or early Mesozoic age. Granularity commonly is coarse and colors range from white to shades of gray. Masses of dense, fine-grained rock are rare in this area. Dolomite and magnesian limestones are present in the exposures on Necnach quadrangle east of Lebec, but elsewhere the magnesium content tends to be low. Silica or silicate minerals have been introduced locally into some deposits by contact metamorphism and for some uses such limestone must be selectively mined. Deposits in the Tehachapi Mountains support two industrial plants, one at Monolith and one at Mojave.

In the Victorville-Oro Grande district of southwestern San Bernardino County, limestone, dolomite, and dolomitic limestone are all found in commercial quantities.

These may occur singly or together in a given deposit and in places are interbedded with other metasediments such as mica schist, quartzite, and hornfels. The carbonate rocks come in the Upper Paleozoic Oro Grande series and also in the conglomerate member of the Permian Fairview Valley formation (Bowen, 1954, p. 36). A majority of the carbonate masses of the district consist of strongly metamorphosed, coarsely crystalline rock, but there are a few bodies of weakly metamorphosed, dense, fine-grained rock of notable size at Sparkhule Hill and Black Mountain. Limestone ranges from pure white to nearly black, but white and gray or variegated combinations of the two colors are commonest. The Victorville-Oro Grande district ranks among the largest limestone producers in the state but only a little dolomite and dolomitic limestone has been marketed thus far from the district because of small demand.

There are immense reserves of limestone and magnesian limestone in the northern part of the San Bernardino Mountains of San Bernardino County. These rocks are elements of the Furnace limestone which is at least partly equivalent in age and lithology to the Oro Grande series of the nearby Victorville-Oro Grande district. In general these rocks are strongly metamorphosed and coarsely crystalline, but there are some patches of finer-grained, dense, more weakly metamorphosed rock. White and blue-gray hues prevail and select white rock is in demand for white filler and roofing granules. White rock has been quarried intermittently in the Cushenbury district for many years, and during 1956 a cement plant was being constructed near the mouth of Cushenbury Canyon.

Roof pendants of Triassic or Paleozoic age supply crystalline limestone to cement plants and other consumers in the Los Angeles area. Slover Mountain near Colton has supplied enormous tonnages of limestone continuously since 1895. The pendants are embedded in large masses of granitic rock and most of the limestone is coarsely crystalline. White, glassy and blue-gray colors prevail. Deposits in and adjacent to the Jurupa Mountains supply two cement plants, and chemical-grade, agricultural and other grades of limestone are also produced in quantity. Several large, hitherto undeveloped deposits exist in the northern San Jacinto Mountains between the Beaumont-San Jacinto axis and Hemet, but opposition by resort interests and subdividers together with the remoteness of some of the deposits from markets has hindered their development.

The rapid population growth in the San Diego area has increased the demand for limestone products in San Diego and western Imperial Counties. The larger deposits occur in the Jacumba vicinity of southeastern San Diego County, whence they extend down into Mexico, and in the Dos Cabezas district and Coyote Mountains of southwestern Imperial County. The Jacumba and Dos Cabezas occurrences consist of coarsely crystalline limestone and magnesian limestone of undetermined, possibly Triassic, age in small pendants in granitic rocks. In the Coyote Mountains there are large masses of limestone, magnesian limestone and dolomite in an old crystalline complex of Paleozoic or early Mesozoic age. Overlapping this crystalline complex are smaller shell-limestone masses of Miocene age interbedded, interfolded and mingled with Tertiary volcanic rocks and continental sediments. Presence of considerable magnesium in the





FIGURE 5. Processing plant at Kaiser Aluminum and Chemical Company's Natividad, Monterey County, operation. Crystalline dolomite of probable Paleozoic age is calcined to magnesite or ground and sized for roofing granules. *Photo by Cal Pictures, courtesy Kaiser Aluminum and Chemical Corporation.*

carbonate rocks of the crystalline complex is to be expected in many places, and overburden of Tertiary rocks as well as the structural complexity of the Coyote Mountains have to be considered in developing the Coyote Mountain deposits. A small tonnage of dolomite has been quarried in the northwestern part of the Coyote Mountains in the past and the pure-white crystalline limestones of the Jacumba area are being actively exploited

for a number of chemical, agricultural and construction uses.

Immense reserves of carbonate rocks suitable for commercial use occur in the desert mountains of Riverside, San Bernardino and Inyo Counties. These have remained largely undeveloped because of their remoteness from marketing centers. However, a few of these are put into operation each year and intermittent produc-



tion in past years has been substantial. A very large, uniform deposit of limestone was developed during 1955 as a source of carbon dioxide and lime. It occurs in marine sediments of Carboniferous age in the Argus Range north of Searles Lake. Paleozoic limestones and marbles are quarried from time to time in the Keeler district of Inyo County and in the Ivanpah, Chubbuck and Marble Mountains districts of eastern San Bernardino County.

Marl deposits have been worked intermittently in California at widely scattered points. None of them are known to be extensive and the calcium carbonate content varies widely within the deposits and from deposit to deposit. Most of them are of evaporite, or caliche type, but some of the materials that have been marketed as marl in California are actually shell-bearing sedimentary rocks, either shales or sandstones. Still others are soils and weathered sedimentary rocks impregnated with hot-spring-derived carbonate material. Shell-bearing shales or loosely consolidated sandstones have been quarried for cement near Napa, Napa County, near Edenvale, Santa Clara County, for agricultural purposes, and near Benicia, Solano County, for cement. Mixtures of weathered sediments and hot-spring travertine have been utilized for cement at Cement, Solano County, and Cowell, Contra Costa County. Caliche-type marls are found principally in the Minkler district east of Fresno County, in the Mojave desert near Oro Grande and to a minor extent in the Lakeview and Jamul districts of San Diego County and the Madrone district of Santa Clara County. Marly lakebeds of Pleistocene age in the desert near Helendale, San Bernardino County, were quarried intermittently during the 1920's as a source of agricultural minerals.

#### FIELD CHARACTERISTICS WHICH INFLUENCE THE ECONOMIC WORTH OF CARBONATE DEPOSITS

Quite commonly limestone and dolomite rocks are found interbedded in the same formation, in some cases in massive layers that can be mined separately, but in others in intimately interbedded or otherwise intermixed masses that cannot be selectively mined. Mill separation techniques for such mixed materials have been successfully developed for certain mixed deposits in some eastern states but have not proved to be economically feasible in California thus far. Mining of many deposits of crystalline limestone is further complicated by intrusions of igneous rock which disrupt the continuity of the deposit and in many cases add undesirable minerals such as quartz, amphiboles, garnets, pyroxenes and epidote, to the limestone.

Chert (silica in the form of chalcedonic quartz or a mixture of opal and chalcedony) is a troublesome rock commonly associated with Coast Range limestones, particularly in rocks of the Jura-Cretaceous Franciscan group (Calera limestone), and the limestones of the Miocene Monterey formation. Chert is also common in the Permian McCloud limestone of Siskiyou and Shasta Counties and in many limestone formations of the Mojave Desert and Basin Ranges. Generally light gray to dark brown in color, it is easily identified by its dense, horn-like texture and its resistance to weathering. Chert nodules and beds commonly stand out sharply from the limestone matrix on weathered outcrops.



FIGURE 6. Dolomite quarry at Westvaco Chemical Division of Food Machinery Corporation's Hollister, San Benito County, operation. Pure white, crystalline dolomite of probable Paleozoic age is quarried by electric shovels from hill benches. The rock has been so crushed because of proximity to the San Andreas fault that very little blasting is required. Photo by C. W. Chesterman.

Replacement masses of dolomite commonly cut across crystalline limestone bodies in the foothill limestone belt of the Sierra Nevada, in the McCloud limestone of Shasta County, in the Gabilan Range of Monterey and San Benito Counties and in a number of the desert limestone deposits of southeastern California. Replacement dolomite is commonly denser and finer-grained than the host rocks and, as dolomite is less soluble in rain water and groundwater than limestone, presents a characteristic weathered surface that differs considerably from the surrounding limestone. The weathered dolomite surface commonly resembles an elephant's skin, the shallow



FIGURE 7. Quarry faces at Westvaco Chemical's Hollister dolomite quarry. Except for local discoloration by iron-bearing groundwater the rock is uniform, snow-white material. Photo by C. W. Chesterman.



solution pits being arranged in a reticulated pattern that gives a gnarled or wrinkled appearance. The extensive, deep solution-pits generally characteristic of limestones in areas of high or moderate precipitation commonly are absent in masses of replacement dolomite except where inclusions of limestone had been caught in the dolomite.

In many terranes of crystalline metamorphic rocks the carbonate units have been so intimately folded with rocks of non-carbonate nature, such as slate, schist and quartzite that beds that originally would have been of economic value are now too thoroughly intermixed to be profitable to mine.

#### MINING AND PROCESSING METHODS

Most California companys have been able to take advantage of limestone and dolomite deposits situated on hill topography where they can be quarried from level benches driven into the hillsides. In a few places however, it has been necessary to utilize pits sunk well below local base level with resultant higher quarrying costs. There are three large-scale underground mines in California from which limestone and dolomite are obtained, and one large glory-hole operation where the haulage-ways and part of the rock-storage facilities are underground. The underground mines are at Shingle Springs, El Dorado County; Sonora, Tuolumne County; and Crestmore, Riverside County; the glory-hole operation is at Davenport, Santa Cruz County. In past years limestone was mined near Cool, El Dorado County in an immense glory-hole, and limestone has been mined near Felton, Santa Cruz County by room-and-pillar methods.

With few exceptions, California limestone and dolomite deposits are so firm and tenacious that blasting is required in order to break down the rock into fragments of suitable size for handling and processing. Two notable exceptions are the Skyline limestone deposit near Crystal Springs Lakes in San Mateo County and the Hollister dolomite deposit near Hollister, San Benito County. In both of these deposits the rock has been crushed by faulting in or near the San Andreas fault zone so that little or no blasting is required to break the rock.

*Quarrying.* In common bench-quarrying practice 20-, 30-, and 50-foot and even wider bench spacings (vertical distance between floor levels or height of the working face) may be adopted depending upon the topography, the distribution of various grades of rock in the deposit, and other considerations. A line of holes is commonly drilled, at a suitable distance back from the working face, from the top of the face down to the approximate level of the quarry floor. For many years churn and wagon drills were standard drilling equipment and are still widely used. However, the faster, more economical rotary drills have greatly increased drilling efficiency in recent years and are rapidly supplanting gravity and percussion-type drills.

In many California operations, particularly those close to population centers or to transportation lines, it is desirable to blast as infrequently as possible. In such cases coyote-hole blasting has become common practice. By this method crosscut and lateral tunnels are driven into and behind the working face. These are then loaded with explosives and a very large quantity of rock is

broken in a single blast. It is not uncommon to break a million tons or more of rock at a time. The use of large drop-balls has supplanted much of the secondary blasting formerly employed in most quarrying operations. Drop balls are simply tear-drop-shaped masses of steel 1000 or more pounds in weight attached by cable and boom to an electric winch. The ball is raised to a suitable height and dropped onto the pieces of broken rock that are too large for easy handling.

*Underground Mining.* Room-and-pillar, shrinkage stope and block caving methods have all been successfully employed in California limestone mines. U. S. Lime Products Company at Sonora, Tuolumne County employs a modified room-and-pillar method, workings being driven from a vertical shaft. The rooms commonly are 50 feet wide and several hundred feet long. Some reach a height of 50 feet. The deposit is a nearly vertical, tabular mass of carbonate rock about 300 feet wide. It has been developed to a depth of about 300 feet and a strike length of over 1000 feet.

At the El Dorado Limestone Company mine at Shingle Springs, El Dorado County, the shrinkage stoping method is employed. Limestone occurs in two nearly vertical, tabular to slightly lenticular, subparallel masses ranging from a few feet to nearly 50 feet apart. The east mass averages about 60 feet wide and the west, 40 feet wide. Entry to the mine is through a three-compartment vertical shaft 1000 feet deep, the deepest stopes being on the 800-foot level. Completed shrinkage stopes 600 feet long, 70 feet wide and 300 feet high have been developed in the thickest parts of the main mass; others are smaller. Main haulageways to the shaft are 20 feet wide and 8 feet high. Short crosscuts perpendicular to the main haulageway connect with draw points (chutes) from the stopes.

The Crestmore mine of Riverside Cement Company until recently used the block-caving method of mining, entering by a five-compartment, 350-foot vertical shaft. The caved blocks were about 200 feet high, 200 feet wide and 240 feet long. Blocks were isolated by cut-off shrinkage stopes at both sides and ends. The haulage level consisted of parallel drifts driven on 70-foot centers and the mining level consisted of parallel drifts driven on 35-foot centers (Robotham, 1934, pp. 1-20; Tucker and Sampson, 1945, p. 174; Wightman, 1945, pp. 215-224). Access and ore-pass raises connected the mining and haulage levels. Two limestone masses have been worked in the underground mine. These are 200 to 300 feet thick and dip underground at angles between 30° and 45°. The two masses are separated by several hundred feet of granitic rock.

Early in 1954, mining by block caving ceased, and rock was supplied to the cement plant from surface quarries while the new mine was developed. The new mine, placed in operation in 1956, will ultimately reach a depth of 1500 feet. Mining is by the room-and-pillar method, rooms being 60 feet wide, 90 feet high and running the full width of the limestone mass. Rock is removed from the mine via a spiral truck haulageway 30 feet wide and 20 feet high over a 10 percent grade (Persons, 1955, pp. 76-77). Conventional electric shovels are employed for loading.





FIGURE 8. Crushing and sizing and rock storage installation at Westvaco Chemical's Hollister dolomite quarry. Photo by C. W. Chesterman.

**Transportation.** Rock is transported from the quarry to processing plant or to market by truck, rail, belt conveyor or various combinations of these methods. Specially designed rear- and side-dump trucks, trailers and railroad cars are constantly being devised to facilitate transportation and reduce handling costs. Loading is accomplished by electric shovels, gasoline-powered skip-loaders, bucket and belt-conveyors and even by simple bulldozer-and-ramp methods. Where crushing is accomplished at the quarry, storage bins and chute-loading facilities, as well as the crushing and screening installations generally are constructed.

**Processing.** Processing of most limestone and dolomite simply involves crushing and sizing. Where certain trace impurities, such as iron oxide coatings, need to be removed, a washing and scrubbing circuit may be added. In small operations, particularly those that may be temporary, it has become common practice to make use of portable units consisting of a jaw crusher and screens or a jaw crusher, hammer mill, and screens, together with recycling and loading belt- or bucket-type con-

veyors. Several firms make portable units of this sort mounted on wheels.

Where the end-product is to be finely divided, more elaborate equipment is necessary. Various combinations of ball mills, rod mills, tube mills, roll crushers, cone crushers and numerous other devices are employed for secondary and fine grinding (Perry, J. H., et al., 1950 pp. 1120-1146; Pit and Quarry Handbook and Directory, 1955; pp. AA3-AA98; Taggart, A. F., 1945, sections 4, 5 and 6). Sizing may be accomplished by various combinations of rotating screens, vibrating screens, hot dry screening installations, wet screening and wet classification devices, air separators and the like (Perry, J. H., et al., 1950, pp. 922-964; Pit and Quarry Handbook, 1955, pp. AA9-AA160; Taggart, A. F., 1945, sections 8 and 9).

**Manufacture of Lime, Magnesite, Magnesian Lime and Carbon Dioxide.** Calcining (burning) carbonate rocks at temperatures ranging from 545° C. to 1500° C., depending upon the minerals involved and the desired purity of the end-product, converts them to a metallic-oxide (or oxides) and carbon dioxide gas. Carbonate rocks are important sources of metallic oxides and carbon dioxide in California, although in some operations one or more of the end products goes to waste. Under most conditions the temperature at which carbon dioxide begins to be dissociated (driven off) from limestone is about 725° C., but there is some variation because of impurities and because of physical characteristics such as particle size and internal structure of the particles. For example, the temperatures of dissociation of dolomite have been found to be considerably lowered by prolonged grinding (Bradley, F. W., et al., 1953, pp. 207-217).

For most carbonate minerals there is some temperature range at which carbon dioxide gas is given off in greatest volume or there may be 2 or 3 peaks of dissociation as in ankerite or dolomite. For calcitic limestones the major evolution of gas is between 900° C. and 1000° C. A kiln temperature of about 1200° C. is maintained in burning most high-calcium limestones, as well as in burning magnesian limestones having a moderate magnesium content, to insure complete dissociation. The time required to convert limestone to lime at such a temperature depends upon the particle size of the rock being calcined and upon the type of kiln being used. In the old single-charge kilns using wood or charcoal fuel the burning time was as much as 4 days, and the resulting product commonly contained unburned residue. Modern kilns have reduced the burning time to a few hours, operating with more even calcination and leaving very little uncalcined residue.

Pure magnesite is largely converted to magnesia (MgO) and carbon dioxide at temperatures between 545° C. and 835° C., the maximum dissociation effect being at about 700° C. However, a small amount of CO<sub>2</sub> may remain under considerably higher temperatures, and both magnesite and dolomite (of which half the composition can be expressed as magnesium carbonate) commonly are burned at kiln temperatures as high as 1500° C. The dissociation range for pure dolomite has been determined experimentally as 825° C. to 945° C. with maximum effects at 810° C.  $\pm$  15° and 940° C.  $\pm$

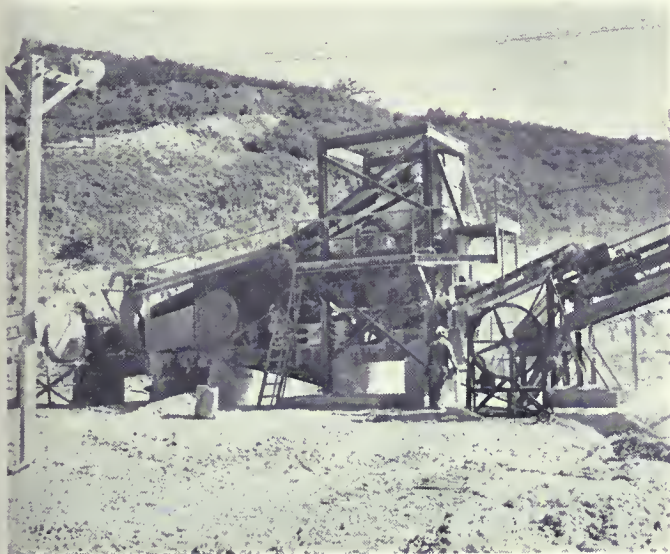


FIGURE 9. Detail of crushing and screening equipment at Westvaco Chemical's Hollister dolomite quarry. Photo by C. W. Chesterman.





FIGURE 10. Limestone quarry west of Gazelle, Siskiyou County. Crystalline limestone of Silurian age is intermittently quarried for agricultural and chemical use, chiefly for the Oregon market.

25° (Haul and Haystek, 1952, pp. 166-179). End-products of calcination of both magnesite and dolomite vary, in density and other physical characteristics, with the intensity and speed of calcination employed. Consequently, the kiln practice changes in processing of magnesite and dolomite whereas calcination of limestone is a less complicated, more nearly fixed procedure. Inasmuch as the dissociation reaction is reversible, that is the liberated gas can re-combine with the metallic oxides, particularly under increased pressure, the processing plant must be so designed as to draw off the carbon dioxide gas as soon as it is liberated.

Two general types of kilns are commonly used in California, the vertical or shaft type and the rotary. Stone to be calcined in the vertical type of kiln, the type commonly found in sugar refineries, must hold its lump shape during calcination to allow circulation of the hot gases in the kiln. Most crystalline carbonate rocks, particularly the medium and coarsely crystalline varieties cannot be used in this type of kiln. No such requirement applies where rotary kilns are employed, but the fuel consumption is greater. Limestones and magnesian limestones that yield as little stony residue as possible after calcination are the most desirable for burning to lime, but rock containing nodules or small masses of silica, or silicate aggregates, that can be readily screened out of the calcined material, has been utilized when available at lower cost.

Because of its affinity for water and for carbon dioxide, and because heat is given off during hydration and carbonatization, the kiln-discharge products (quicklimes) are hard to handle. In California, the market for quicklime is small and most lime is sold in hydrated form (chiefly calcium hydroxide or calcium and magnesium hydroxides). Hydrated limes are much more stable under atmospheric conditions than quicklimes and do not require special processing and handling equipment. Quicklime is commonly hydrated, after crushing to minus 1-inch size and screening out impurities, in shallow, closed pans by introduction of water. Water is added, the pan is rotated and the bottom is continuously scraped until evolution of steam ceases and the contents become light and dry. Ordinarily, about 18 pounds of water must be added to 56 pounds of high-calcium lime to

make hydrated lime of the proper consistency (Bowles, 1952, p. 38). Overslaking leaves the lime wet and sticky.

High-calcium limes slake considerably faster and liberate more heat than limes containing considerable magnesia. They also hydrate more completely than magnesian (dolomitic) limes. Under simple procedures, dolomitic lime hydrates to a mixture of calcium hydroxide and magnesium oxide with little or no magnesium hydroxide. Such material behaves erratically when used in mortars and plasters. Conversely, dolomitic lime when treated in an autoclave (pressurized chamber) under considerable pressure hydrates evenly, has special advantages of workability and appearance over high-calcium lime and is an important building material. There is considerable variation in the design of calcining and hydrating equipment and the processes are carried out under carefully controlled conditions. In general, no single type or design of hydrator is suitable for making all kinds of lime (Bowles, 1952, p. 38) so that a complete installation for production of all the various kinds of lime is complex and expensive.

#### MARKETING OF LIMESTONE, DOLOMITE AND LIME PRODUCTS IN CALIFORNIA

*General Considerations.* Limestone and dolomite are both low-priced commodities which must be produced reasonably near to centers of consumption or transportation costs become prohibitive. With but few exceptions, limestone and dolomite are produced within 150 miles of consuming centers. The one exception insofar as California is concerned is U.S. Lime Products' operation in and near Henderson, Nevada which supplies limestone and dolomite to southern California. This Nevada rock is a non-decrepitating variety used by sugar refineries and steel mills which require material that will retain a lump shape during calcination. Rock having this characteristic was not being produced in southern California in 1956.

There are also a few scattered, intermittently active quarries which operate under special conditions. For

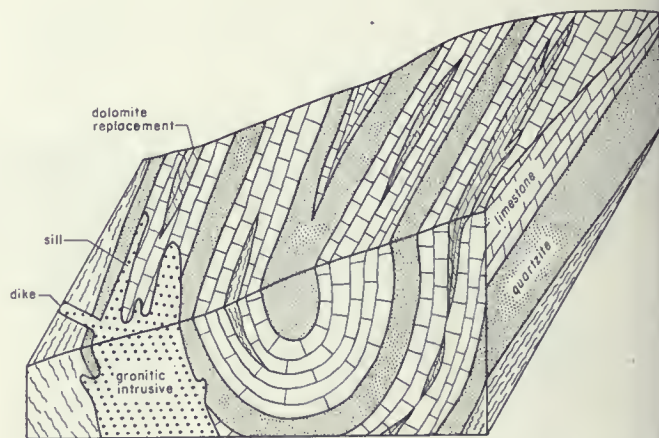


FIGURE 11. Block diagram of a typical California limestone deposit. The limestone-bearing series consists of interbedded schist, quartzite, and limestone which have been folded into a tight syncline or trough pitching away from the observer. The lower limestone member has been partly replaced by dolomite and the left limb of the structure invaded by a small stock of granitic rock which has sent out satellitic dikes and sills into the metamorphosed sediments.



example, the limestone quarry at Lime Mountain, San Luis Obispo County, supplies sugar refineries in Salinas Valley, and the Minkler district marl deposits near Fresno supply agricultural material to farmers in the Fresno area. Los Angeles and San Francisco are the most important marketing centers and most limestone and dolomite quarries are clustered around these focal points. At present almost all of the limestone and dolomite produced in California is consumed here, although some specially processed materials such as whiting and fillers are shipped as far as Canada.

In the case of large limestone-quarrying operations, such as those connected with portland cement plants, the cost of quarrying, primary crushing and transporting the rock from deposit to processing plant is accomplished as low as 25 cents per ton. Cost of mining limestone in smaller quarrying operations and in underground mines may run well over a dollar a ton. Large installations utilizing belt conveyors can transport rock as low as 2 cents per ton-mile whereas short-haul trucking can hardly be done cheaper than 7 or 8 cents per ton-mile because of the cost of loading and unloading. Freight rates from the margin of the 150-mile producing perimeter around the San Francisco and Los Angeles marketing centers range from about 2 dollars to 4 dollars or slightly more per ton.

An individual contemplating putting a limestone or dolomite property into operation is faced with several alternatives. He may quarry, process and market the rock himself; lease his property to others on straight lease or lease and royalty agreement; or sell his property outright. He may also carry on any of the three phases—quarrying, processing or marketing and delegate the others to concerns better able to carry them forward. Selling or leasing generally involves little or no capital outlay for the owner, whereas any phase of producing or marketing a product may entail a large capital outlay. Among the smaller operators who have avoided large capital expenditures are those employing portable crushing-sizing-loading units which are either rented or leased by the operator or are purchased under long term financing. Lime plants all require considerable capital outlay and portland cement plants cost 12 dollars or more per barrel of annual rated capacity.

**Prices.** Prices obtained for limestone and dolomite on the open market vary broadly depending upon the degree of processing necessary, the chemical and physical character of the rock, the demand for the particular

variety being offered and the competition among producers. In short, the price structure is a complicated one governed by numerous special conditions. Large-scale consumers are generally able to negotiate lower prices with the producers than small buyers. During the period 1950-56, sellers of limestone having a calcium carbonate content of 96 to 98 percent, or better, have received about \$3.00 per ton upon the average (f.o.b. quarry or railroad) for quarry-run or crudely sized rock (i.e. sizes such as plus four-to minus six-inch). The lowest prices recently received for limestone and dolomite are slightly less than \$1.00 per ton for rock intended for road base, concrete aggregate, or asphalt mix where a moderate degree of chemical inertness and considerable strength are the only requirements. The highest prices obtained for quarry-run or crudely sized limestone in recent years have been paid by the sugar refineries for exceptionally pure, tenacious varieties that are particularly well-suited to the sugar refining process, and by manufacturers of white filler who require rock of exceptionally uniform white color in addition to rigid chemical specifications. These premium varieties have sold as high as \$5.00 or more per ton exclusive of transportation costs.

Limestone and dolomite products of exceptional uniformity in small particle sizes that meet rigid color, absorption and reflectance requirements sell at much higher prices than quarry-run or crudely sized materials. For example, limestone of high purity (98 percent  $\text{CaCO}_3$ ) and high degree of whiteness, air-separated to micron sizes or even fine-ground to minus 325 mesh, may bring prices ranging from \$15.00 to \$25.00 or more per ton. Packaging of such material costs an additional \$3.00 to \$4.00 per ton or even more.

Most of the dolomite produced in California and a major proportion of the limestone is captive tonnage, that is, the quarrying, processing and selling is done by a single operator. He does not normally state the value of the crude rock in his report to statistics—gathering agencies and such rock is never quoted as an open market item. Consequently, the foregoing prices apply only to open-market quotations.

#### UTILIZATION OF CARBONATE ROCKS IN CALIFORNIA

**History.** The use of lime-bearing materials in California dates back to the building of the Spanish missions where whitewash and lime mortars were widely used in small quantities. Abalone shells obtained on the beaches

Table 1. Principal uses of limestone in California in 1955 in approximate order of amount used.\*

Use	Amount of limestone used	Value of limestone	Value of finished product
Portland cement.....	9,000,000 tons	Captive tonnage. Value not indicated	\$103,305,000
Aggregate, railroad ballast, road metal, riprap and allied crushed rock products	1,000,000 tons	\$1,200,000	
Lime, including magnesian lime and calcined dolomite.....	500,000 tons		4,000,000
Sugar refining.....	250,000 tons	890,000	
Steel flux†.....	92,945 tons	298,310	
Roofing granules.....	63,000 tons	425,000	
Agricultural (including stock feed and fertilizer filler).....	82,000 tons	517,000	
Miscellaneous (glass, fillers, whiting, stucco, acid neutralization, explosives, oil-well drilling, etc.)	170,000 tons	1,165,000	

\* All limestone consumed in California is produced within the state except for a substantial part of the rock used in sugar refining and as steel flux which comes into the state from Nevada. The tonnages are estimated.

† Does not include production of one Nevada operator who markets in California.



Table 2. *Some of the uses for dolomite and magnesian limestone.***Magnesium Refractories and Chemicals**

Dead-burned dolomite  
Periclase brick  
Chrome-magnesia brick  
Magnesium oxide  
Hydrated magnesia  
Magnesia pharmaceuticals  
Magnesium chemicals

**Construction Industries**

Aggregate, railroad ballast, road met l  
Roofing granules and terrazzo chips  
Magnesian lime for plaster

**Agriculture**

Soil conditioner  
Animal and plant food  
Ingredient in insecticides and fungicides

**Miscellaneous Uses**

Manufacture of glass  
Source of carbon dioxide  
Source of metallic magnesium

was probably the first material burned into lime. Later, accumulations of fossil shells were found and finally the crystalline limestones were discovered and used locally. Not until the gold rush days of the early 1850's did lime become important in the construction industry, but from then on hundreds of lime kilns sprang up all over California. The rise in demand for lime was directly related to the hazardous fires which repeatedly swept through towns made of frame buildings. Field stone or brick buildings laid up in mud or lime mortar became the standard type of construction throughout the gold country and many of these remain in use today. A great deal of lime was imported from Europe to supply the demand during the early part of the gold rush period.

The lime-burning business probably had its heyday between 1880 and 1900—in relation to its importance to the current economy if not in actual tonnage produced. Vast banks of lime kilns were constructed in the Santa Cruz Mountains, Santa Lucia Mountains, Sierran foothills, Tehachapi Mountains, and southwestern San Bernardino County. Many of these lime companies were as significant for their day as the portland cement companies now are—in relation to the rest of the economy.

Although portland cement was invented in England as early as 1825, it was not used to any great extent in California until the late 1850's and 1860's. The first cement used here was imported from Europe. Even then its use did not greatly supplant lime mortars nor did concrete become serious competition to masonry construction until about the turn of the century. Cement manufacturing in California dates back to 1860 when a hydraulic cement (a type manufactured at considerably lower temperature than portland cement) was placed on the San Francisco market. This was made at Benicia, Solano County, from travertine and clay. The first cement approaching the true portland type was made at Santa Cruz about 1877, from crystalline limestone and clay. Another early plant that produced a portland-type cement was built on the Jamul Ranch, San Diego County, in 1891. Since the early 1900's, cement plants have been the largest consumers of limestone in California, but numerous other industrial uses of limestone are equally important to the economy of California even though the quantity of material they consume is smaller.

Table 3. *Some of the many uses of lime.***Chemical Industries**

Source of calcium and carbon dioxide in the manufacture of other chemicals:  
Caustics and alkalis  
Calcium carbide, calcium bisulfite, calcium cyanamide, etc.  
Vehicle in base exchange in manufacture of such products as magnesium salts  
Neutralizer of acids  
Catalytic agent in numerous processes  
Dehydration of such materials as alcohols and petroleum products  
Precipitating and coagulating agent  
Hydrolizing agent in glue, rubber and paper-pulp manufacturing  
Saponification of fats and oils in manufacture of calcium soaps  
Oxidizing and reducing agent in various processes  
Gas absorbent  
Solvent, as in tanning of hides and smelting of metals

**Construction Industries**

An ingredient in:  
Lime mortar  
Plaster  
Stucco  
Paint pigment  
Sand-lime and silica brick  
Rock wool

**Filler in:**

Asphalt-base roofing  
Asphalt tile  
Linoleum

**Additive in concrete, increasing:**

Waterproofing characteristics  
Workability (plasticity)

**Agriculture**

Plant food  
Neutralizer of acid soils  
Coagulant or flocculant in clay soils  
Ingredient in insecticides and fungicides  
Filler in insecticides and fertilizers  
Animal food  
Animal sanitation  
Food preserving

**Mining and Metallurgy**

Flux in ferrous or non-ferrous metal reduction  
Flux in manufacture of ceramic products  
Scavenger of sulfur and phosphorus in steel manufacture  
Acid neutralizer in ore dressing  
Dusting in coal mines to reduce fire hazard  
Whitening of mine walls

**Miscellaneous Industries**

Manufacture of soap  
Manufacture of glue  
Manufacture of bleaching powder  
Manufacture of varnish and paint  
Manufacture of rock wool  
Manufacture of glass  
Manufacture of paper  
Manufacture of refractories  
Refining of sugar  
As disinfectant

Dolomite was probably first used in California as a building stone. Dolomite marble dimension stone was first produced commercially in Inyo County about 1888. Production of dolomite in California was intermittent and not large up to 1942. Except for durable material used as crushed stone, the commonest use for dolomite up to 1942 was as a basic flux in the manufacture of steel. In 1942 the Henry J. Kaiser interests initiated the use of dolomite in the manufacture of magnesia refractories. Within the following decade the other California producers of magnesia altered their processes in order to use dolomite so that these firms are by far the largest users of dolomite in California at present (see section on magnesium and magnesium compounds in this volume). Prior to the advent of the use of dolomite in the manufacture of magnesia it had been made by interaction of lime with sea water. Interaction of calcined dolomite with sea water gives a substantially larger yield of magnesia.



Table 4. Specifications for limestone and dolomite and lime for the principal consuming industries.\*

Use	Chemical requirements	Physical requirements
Limestone for portland cement.....	Magnesium oxide (MgO) not more than 3%, preferably not more than 2%. Total alkalis not more than 0.5%. Minimum calcium carbonate (CaCO <sub>3</sub> ) content varies from plant to plant depending upon availability of other raw materials.	
Limestone for lime (high calcium).....	Calcium carbonate (CaCO <sub>3</sub> ) content not less than 97%, preferably 98% or more.	Some manufacturers prefer limestone that does not decrepitate during calcining, i.e., that will hold its lump form throughout calcination.
Magnesian limestone for lime (magnesian)...	Magnesium oxide (MgO) content should fall between the limits of 10 and 15%, preferable 11-12%.	Some manufacturers prefer rock that does not decrepitate during calcining.
Limestone and magnesian limestone for steel flux (blast furnaces)	Silica (SiO <sub>2</sub> ) less than 5%. Alumina (Al <sub>2</sub> O <sub>3</sub> ) less than 2%. Magnesia (MgO) less than 4% to less than 15% at various plants. Phosphorus pentoxide (P <sub>2</sub> O <sub>5</sub> ) not more than a trace, i.e., .005 to .006.	Some manufacturers specify rock that will not decrepitate when heated.
Limestone for steel flux (open hearth).....	Calcium carbonate content preferably more than 98%, lower grades occasionally accepted. Phosphorus must not exceed trace amounts.	Some manufacturers specify rock that holds its lump form until consumed in the melt.
Dolomite for refractories.....	Magnesium oxide (MgO) not less than 18%. Silica (SiO <sub>2</sub> ), ferric oxide (Fe <sub>2</sub> O <sub>3</sub> ) and alumina (Al <sub>2</sub> O <sub>3</sub> ) not to exceed 1% each, but lower grades sometimes accepted.	
Limestone for general chemical use.....	Calcium carbonate content should exceed 98%. Preferred rock runs more than 99% CaCO <sub>3</sub> . Limestone as low as 97% CaCO <sub>3</sub> is sometimes accepted.	Some manufacturers require rock that will not leave a scum when dissolved in acid.
Limestone for beet-sugar manufacturers.....	Silica (SiO <sub>2</sub> ) not more than 1%. Magnesia not more than 4%. At some plants ferric oxide (Fe <sub>2</sub> O <sub>3</sub> ) must not exceed 0.5%.	To be acceptable at most California plants limestone must retain its lump form during calcination (burning).
Agricultural limestone.....	In general the higher the lime (CaO) content the better the price. Rock containing less than 85% CaCO <sub>3</sub> is seldom accepted.	Other factors being equal, a soft, friable rock is more acceptable because it is cheaper to process.
Agricultural dolomite.....	The price received is dependent mainly on the calcium-magnesium carbonate content, rocks being seldom accepted if they contain less than 85% of carbonate minerals.	Same as agricultural limestone.
Limestone and dolomite for glass.....	Ferric oxide (Fe <sub>2</sub> O <sub>3</sub> ) not more than 0.05%, preferably not more than 0.02%. Calcium carbonate (CaCO <sub>3</sub> ) content should exceed 98% in case of limestone, or 98% calcium-magnesium carbonate, in case of dolomite.	
Limestone for calcium carbide and calcium cyanamide	Calcium carbonate (CaCO <sub>3</sub> ) content must exceed 97% and should exceed 98%. Magnesium oxide (MgO) should be less than 0.5%; alumina and ferric oxides (together) less than 0.5%; silica (SiO <sub>2</sub> ) less than 1.2%; and phosphorus, less than 1.2%. Sulfur must not be present in greater than trace amounts.	Rock must retain its lump form during calcination.
Limestone for paint and filler.....	In general the calcium carbonate content should exceed 96% but magnesian limestones containing as much as 8% magnesium oxide are (rarely) tolerated—the MgCO <sub>3</sub> content generally is 1%. Other maxima are: Fe <sub>2</sub> O <sub>3</sub> -0.25%, SiO <sub>2</sub> -2.0% and SO <sub>3</sub> -0.1%.	Rock which breaks down into rhombic particles is preferred in some plants. The main controlling characteristic is the degree of whiteness shown by the processed material.
Limestone and dolomite for concrete aggregate, ballast, road metal, road base	Concrete aggregate should be low in alkalis and free of surface organic matter. Presence of opaline silica is highly undesirable in concrete aggregate. Other aggregate suitability is based chiefly on durability, particularly toughness.	Must be clean, strong, durable and of low porosity.
Quicklime for pulp and paper manufacturers	Calcium oxide (CaO) contents must be more than 96% for most manufacturers.	
Lime for soft rubber goods.....	Magnesian lime is generally used. Must be free from carbonates and should contain less than 3% of total impurities other than carbon dioxide or magnesium oxide. In vulcanization such lime must also be free of manganese, copper and calcium oxides.	Must be thoroughly hydrated, fine-grained and free of grit.
Lime for lubricants (greases).....	Calcium oxide not less than 72.6%, magnesium oxide not more than 1%. maximum silica plus iron oxide plus alumina, 1.5%, maximum carbon dioxide (at point of manufacture), 1%.	Must be completely hydrated and free of grit.
Lime for textile dyeing.....	Calcium oxide (CaO) not less than 94%, alumina-iron not more than 2%, silica not more than 2.5% and magnesia not more than 3%.	
Varnish.....	Must be very low in iron and magnesium oxide.	Must be very fine-grained and very white.

\* This table indicates such chemical and physical requirements as have been standardized by the various consuming industries.

In recent years there has been a considerable production of dolomite for white roofing granules and some has been marketed for agricultural purposes.

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## LITHIUM AND LITHIUM COMPOUNDS

BY WILLIAM E. VER PLANCK

In 1952 the United States produced lithium compounds valued at \$1,052,000 and containing 1,088 tons of lithium oxide ( $\text{Li}_2\text{O}$ ) or the equivalent of nearly 5 million pounds of lithium carbonate ( $\text{Li}_2\text{CO}_3$ ). In California, one company, the American Potash & Chemical Corporation at Trona, San Bernardino County, is recovering lithium carbonate from the brines of Searles Lake. The Trona production is 1 to  $1\frac{1}{2}$  million pounds per year and therefore represents a significant portion of the United States supply. The pegmatites of the Pala district, San Diego County, yielded lithium ores from about 1900 to 1927; and for several years the production was the largest of any lithium-producing district in the United States.

*Mineralogy and Geologic Occurrence.* Lithium is a widespread element, but economic concentrations are sparsely distributed. It is present in sea water, in many mineral springs, and in the waters of a few undrained basins. Although lithia springs were at one time valued for their supposed therapeutic power, the only lithium-bearing brines that have yielded lithium compounds commercially are those of Searles Lake, which contain only 0.048 percent lithium chloride.

Lithium associated with borax and kernite is present in the shale at Boron, Kern County. Lithia ( $\text{Li}_2\text{O}$ ) comprises a fraction of 1 percent of this shale but the lithium mineral has not been identified (Arundale, 1954). Lithium also is present in the bentonitic magnesian clay mineral hectorite, which is mined near Hector, San Bernardino County. The lithia content of hectorite is 1.12 percent (Foshag, 1936).

Lithium ore minerals are few and with few exceptions occur only in pegmatites. None of the ores contain more than about 10 percent  $\text{Li}_2\text{O}$ ; and because of substitution of sodium or potassium for lithium in lithium-bearing minerals, the quantity of lithia is usually less than the theoretical amount.

Three lithium ore minerals have been important in the United States. Lepidolite, the principal ore mineral in the Pala district, San Diego County, California, is a complex silicate of aluminum, potassium, and lithium with fluorine and water. Its theoretical lithia content is 6.43 percent, but lepidolite ore usually contains three to five percent  $\text{Li}_2\text{O}$ . It occurs as a granular aggregate of pale violet flakes that commonly are fine-grained. No large deposits are known in the United States, but lepidolite deposits of great present importance occur elsewhere in the world, particularly Southern Rhodesia.

Spodumene [ $\text{LiAl}(\text{SiO}_3)_2$ ], theoretically containing 8.1 percent  $\text{Li}_2\text{O}$  and actually one to 7.6 percent  $\text{Li}_2\text{O}$ , is at present the most important lithium ore mineral mined in the United States. Common spodumene occurs as whitish, lath-shaped crystals associated with other pegmatite minerals. Some of the crystals are of huge size. One crystal at the Etta mine in South Dakota was six feet in diameter and 42 feet long, one of the largest single crystals known (Schaller, 1916). The deposits of greatest economic importance at present, however, consist of finger-sized crystals of spodumene disseminated through large bodies of pegmatite material. In the Cali-

fornia pegmatites, some of the spodumene occurs as the transparent lilac to pink variety known as kunzite, which is a valuable semi-precious gem stone. Minor quantities of non-gem, altered spodumene have been mined for lithium ore. Most of the spodumene that formed in the pegmatites of California has been partly to thoroughly altered to clay, and now contains less than two percent  $\text{Li}_2\text{O}$ ; much of it contains less than one half of one percent.

Amblygonite [ $\text{Li}(\text{Al}\cdot\text{F})\text{PO}_4$ ], which was also mined in the Pala district, has a theoretical lithia content of 10.1 percent, but ores usually contain about 9 percent. This mineral, which is the richest lithium ore mineral, superficially resembles feldspar but has a higher specific gravity. No large deposits of amblygonite are known.

Most of the lithium that has been recovered in the United States has been obtained from Searles Lake and from two spodumene-bearing pegmatite districts—one in the Black Hills of South Dakota and the other in the Kings Mountain area of North Carolina. Lithium minerals, principally lepidolite, also have been obtained from pegmatites in northern New Mexico as well as in the Pala district of southern California.

Formerly the mining was confined to pegmatite coarse enough to permit hand sorting of the lithium minerals; but in the early nineteen forties, the mining of disseminated spodumene became possible when beneficiation techniques were developed. Large reserves were thus created, and in 1955 all but a small part of the spodumene obtained in the United States was recovered by the treatment of disseminated ore. Most of this ore contained 20 to 30 percent spodumene and 1.5 to 2.0 percent  $\text{Li}_2\text{O}$ . Deposits that contain less than several tens of thousands of tons of material of this type were generally considered not to be of commercial interest. In 1955 the indicated and inferred reserves of  $\text{Li}_2\text{O}$  were estimated at 128,000,000 units (1,280,000 tons) in the Kings Mountain area of North and South Carolina; 9,000,000 units (90,000 tons) in Searles Lake, California; 1,600,000 units (16,000 tons) in the Black Hills, South Dakota; and 200,000 units (2000 tons) at other localities in the United States (Norton and Schlegel, p. 343). The reserve estimates in pegmatites were based on a minimum grade of 1.0 percent  $\text{Li}_2\text{O}$ .

Very large lepidolite-bearing pegmatite bodies in Southern Rhodesia will contribute a large part of the future consumption of lithium in the United States. Late in 1955, the American Potash & Chemical Corporation completed a plant to treat this lepidolite in San Antonio, Texas.

*Lithium Operations of American Potash & Chemical Corporation.* Beginning in 1938, the American Potash & Chemical Corporation has been recovering lithium from the Searles Lake brine in the form of dilithium sodium phosphate ( $\text{Li}_2\text{NaPO}_4$ ). With a lithia content of about 21 percent, the concentrates from Trona are the world's richest lithium raw material. Since 1951 the company has converted the entire output to lithium carbonate, an important lithium compound of commerce.



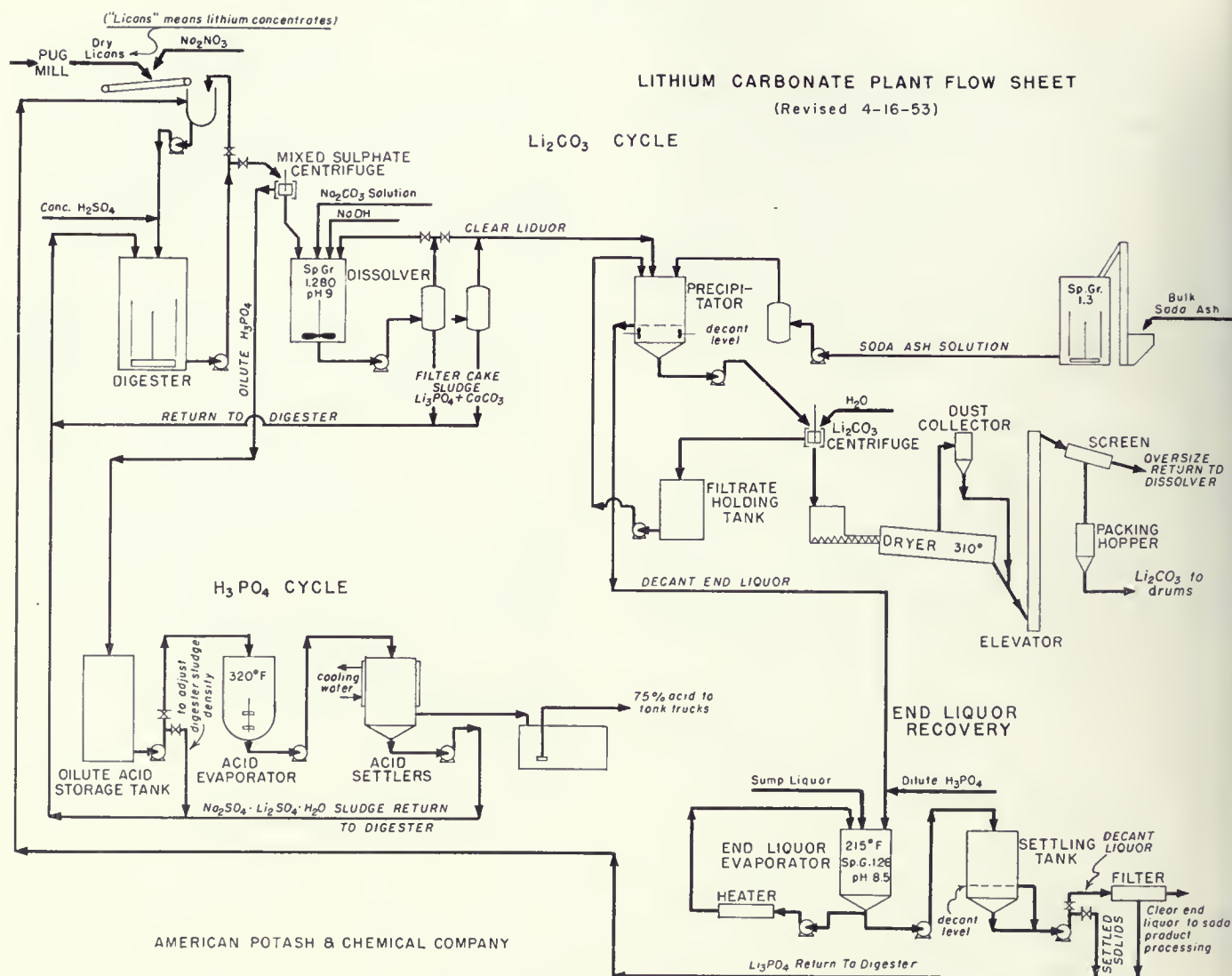


FIGURE 1. Flow sheet, lithium carbonate plant of American Potash & Chemical Corporation, Trona, San Bernardino County.

Lithium is one of the minor constituents of the Searles Lake brine, which is a complex alkali brine containing principally sodium and potassium chloride, borate, carbonate, and sulfate. This brine contains the equivalent of only 0.017 percent  $\text{Li}_2\text{O}$  by weight.

In the main plant cycle, the brine is evaporated in triple effect evaporators, and the concentrated liquor is further treated for the recovery of potash, borax, and bromine. During the evaporation, sodium chloride and burkeite ( $2\text{Na}_2\text{SO}_4 \cdot \text{Na}_2\text{CO}_3$ ) crystallize and are withdrawn from the evaporators as solids. The sodium chloride is returned to the lake, and the burkeite goes to the soda products process for separation into sodium carbonate and sodium sulfate.

Within the evaporators, heat and the concentration of the brine result in the crystallization of insoluble dilithium sodium phosphate ( $\text{Li}_2\text{NaPO}_4$ ). The lithium salt precipitates in the form of particles only 2.5 microns in diameter that are withdrawn from the evaporators with the burkeite. When the soda products plant was put in operation in 1934, troublesome slimes and scums, which were found to be high in lithium, appeared in some

of the equipment. Recovery of lithium came in 1938 and consisted at first of processing slimes collected in various parts of the soda products plant. In 1944, a flotation plant was completed that not only recovers a high proportion of the lithium in the raw brine but also furnishes the soda products plant with clarified feed.

In the present operation, burkeite with entrained  $\text{Li}_2\text{NaPO}_4$  is leached of free sodium carbonate and then dissolved to yield a burkeite solution containing  $\text{Li}_2\text{NaPO}_4$  in suspension. Heat liberated in dissolving the burkeite is removed by aeration in a cooling tower. The burkeite solution goes to the lithium flotation plant; and after the lithium has been removed, the clarified burkeite liquor is returned to the soda products plant for further processing. Flotation agents are a light mineral oil and also a fatty acid derivative used to control frothing in the main evaporators. Air entrained in the burkeite cooling tower causes the frothing in the flotation tanks that is necessary for flotation.

Flotation is accomplished in four cylindrical tanks, each of 10,000 gallons capacity, that are operated in parallel. Each tank is fed at the bottom, and the liquor



overflows into an inner cylinder with a conical bottom. Entrained air forms bubbles that collect the lithium mineral and rise to the surface to form a froth that overflows into a peripheral launder. The froth is collected, deaerated by heating to 150° F., and diluted to dissolve traces of burkeite that may be present. The lithium slurry is dewatered on Sweetland filter presses, a water displacement wash is applied, and the cake is dried. This was the material that formerly was marketed as Trona concentrates. The flotation plant has a capacity of 150 tons of  $\text{Li}_2\text{NaPO}_4$  per month.

The lithium carbonate plant has some of the features of a pilot plant, and equipment formerly used for making bromides has been adapted. Although the process has been worked out and production has reached 100 percent of the planned capacity, numerous refinements are contemplated. It is a batch plant because the scale of operations do not warrant continuous methods.

In brief, the process consists of treating the  $\text{Li}_2\text{NaPO}_4$  concentrate with sulfuric acid and obtaining mixed sulfates of lithium and sodium plus phosphoric acid. Lithium carbonate is precipitated by adding sodium carbonate to a solution of mixed sulfates, and the tail liquor is essentially sodium sulfate.

The lithium carbonate plant consists of three main parts; the lithium carbonate cycle, the phosphoric acid cycle, and the end liquor recovery section. In the lithium carbonate cycle, lithium concentrates brought from the flotation plant, together with concentrated sulfuric acid, are fed into the digester, a large cylindrical tank. Weak phosphoric acid is circulated through the digester to control pulp density. The products of the reaction, a sludge of mixed sulfates of lithium and sodium plus

weak phosphoric acid, are pumped out and separated by centrifuging. The phosphoric acid, which still contains some lithium, is sent to the dilute acid storage tank.

The mixed sulfates are dissolved in water, and residual phosphate is caused to precipitate by an adjustment of pH. The solution is filtered, and the filter cake, lithium phosphate plus calcium carbonate that probably originates in the fresh water added, is returned to the digester. The clear solution of mixed sulfates and a sodium carbonate solution are mixed together to precipitate lithium carbonate. The lithium carbonate is recovered by centrifuging and dried at 310° F. in a steam-heated rotary drier. This completes the lithium carbonate cycle.

In the phosphoric acid cycle, acid from the mixed sulfates centrifuge is collected as already mentioned. One portion of the acid is recirculated through the digester, and the remainder is concentrated by evaporation at 320° F. The hot concentrated acid then goes to water-cooled acid settlers where residual lithium and sodium settle out in the form of a sludge of mixed sulfates. This sludge is returned to the digester. The final product is phosphoric acid of 75 percent grade.

The end liquor recovery involves the removal of all lithium from the lithium carbonate centrifuge filtrate. The filtrate is evaporated at 215° F., and dilute phosphoric acid is added to precipitate the lithium as lithium phosphate. The lithium sludge is returned to the digester. The final end liquor, which is a clear solution rich in sodium sulfate, contains only 0.1 percent lithium. The end liquor is routed to the soda products plant for recovery of values contained therein.

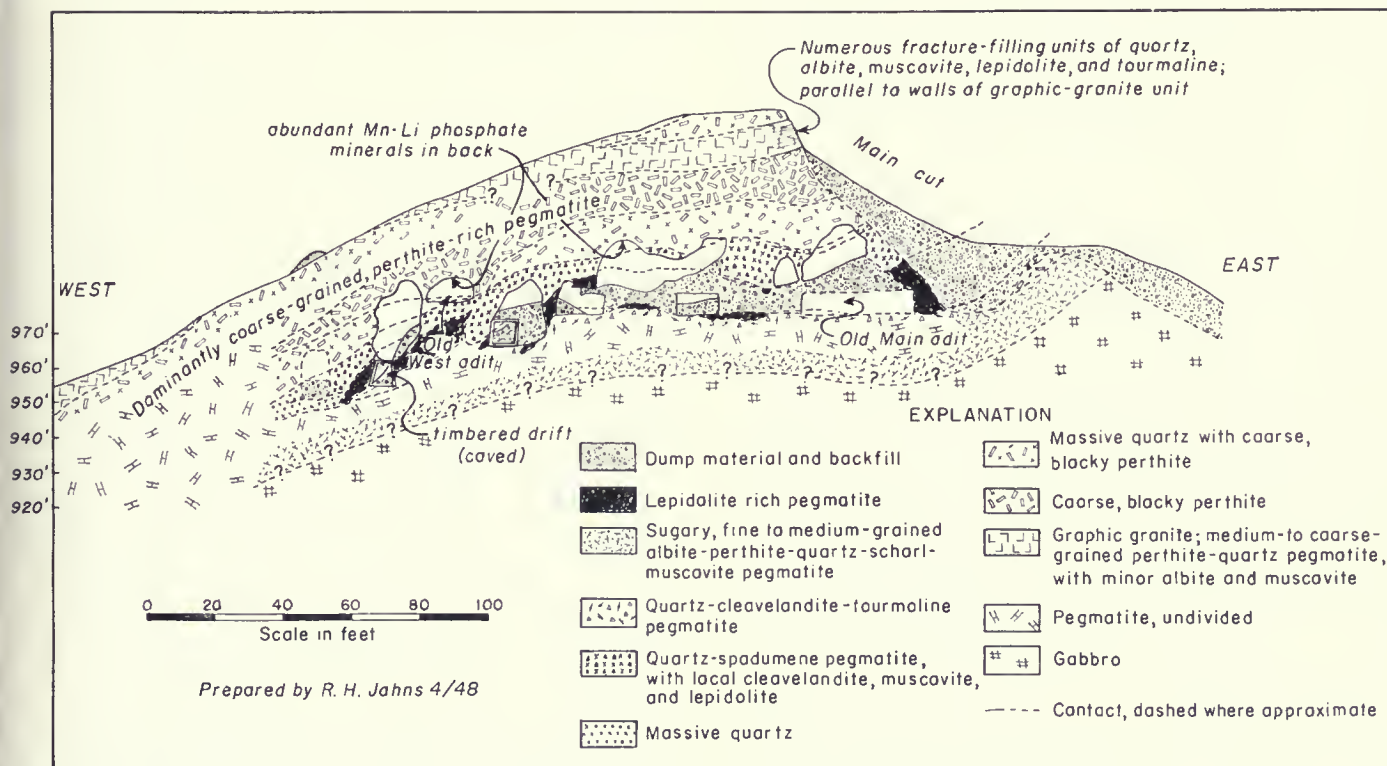


FIGURE 2. Geologic section through Stewart mine, Pala, San Diego County.



*Pala District, San Diego County.* Previous to the first commercial recovery of lithium from Searles Lake, lithium minerals had been obtained from a group of pegmatite dikes in the vicinity of Pala, San Diego County. Though lithium-bearing gem stones (see section on gem stones in this volume) have been produced from numerous mines in the area, a single property, the Stewart mine, has yielded most of the lithium for commercial purposes (Jahns and Wright, 1951). The known commercial concentrations of lithium-bearing minerals are confined to a bulge in an elongate pegmatite dike. The bulge, which is approximately 80 feet thick, contains a discontinuous quartz-spodumene core in its central portion. About the core several pegmatite zones are arranged in layers. Most of the lepidolite-rich pegmatite occurred in two bodies which occurred along the footwall of the core and at or near a bench-like roll in the dike. Each was about 200 feet in maximum dimension.

The Stewart mine was opened in 1892 and was worked sporadically until 1928. Though lepidolite was its principal ore mineral, small amounts of amblygonite also were obtained. The recorded output of these two minerals in the Pala district totals 23,480 tons valued at \$432,800. Virtually all of it was obtained at the Stewart mine. Several of the yearly outputs of this mine were the largest of any lithium mine in the United States. In recent years the mine has been inactive. Much smaller amounts of lepidolite have been obtained from other pegmatites in the area, principally those at the Pala Chief, Vanderburg-Katerina, Tourmaline King, and Tourmaline Queen mines.

*Methods of Recovery.* Four companies, the American Potash & Chemical Corporation, the Foote Mineral Company, the Lithium Corporation of America, and the Maywood Chemical Works, produce most of the lithium concentrates and chemicals recovered from pegmatite minerals in the United States. The Trona plant of the American Potash & Chemical Corporation, which is described above, does not consume lithium minerals; but a subsidiary, the American Lithium Chemicals, Inc., produces lithium hydroxide at San Antonio, Texas, from African lepidolite. The Foote Mineral Company mines spodumene near Kings Mountain, North Carolina, and processes it into lithium carbonate at Sunbright, Virginia, and into other lithium compounds at Exton, Pennsylvania. It also imports lithium ore minerals from Africa. The Lithium Corporation of America produces lithium hydroxide near Bessemer City, North Carolina, from spodumene mined from its deposits near Kings Mountain and from Canadian spodumene. It also produces lithium metal and compounds near Minneapolis, Minnesota, and owns deposits of spodumene in the Black Hills, South Dakota, that were worked through 1955. The Maywood Chemical Works produces lithium metal and compounds of NF (National Formulary) grade at Maywood, New Jersey. This plant consumes spodumene from the company's Etta mine, South Dakota, as well as purchased spodumene.

Spodumene ores can be beneficiated by flotation, but hand picking is the only method for upgrading the other lithium minerals. One company is reported to have 8,000,000 tons of proved and indicated ore (Chem. Eng.

News, 1954), and the other producers also own or control large reserves. From a single operation, ore containing 20 percent spodumene (1 to 3 percent  $\text{Li}_2\text{O}$ ) is being mined by open pit methods at the rate of as much as 1,200 tons a day. Lithium minerals are also obtained from smaller but richer deposits by underground mining methods, and additional amounts are recovered as by-products from the mining of pegmatite minerals such as feldspar and quartz.

The extraction of lithium chemicals from their ores is relatively difficult and expensive. In the process used by the Lithium Corporation of America, spodumene is caused to decrepitate by calcination at  $1000^\circ$  to  $1100^\circ \text{C.}$ , and sulfuric acid is added. By a base exchange process, hydrogen from the acid is substituted for the lithium of the silicate. Lithium sulfate in solution is then extracted from the treated mass by leaching with water, and pure lithium carbonate is precipitated from the solution with soda ash. In the Foote Mineral Company's process, a slurry of spodumene and limestone is calcined in a 10-by 340-foot kiln. Soluble lithium hydroxide is leached from the calcined mixture with water, and the lithium-rich liquor is evaporated to yield crystals of lithium hydroxide. American Lithium Chemicals Inc. calcines a mixture of ground lepidolite and limestone in a rotary kiln. Soluble lithium and potassium salts are leached from the kiln product with water, and lithium hydroxide is recovered from the resulting solution by evaporation, filtration, and drying.

*Properties of Lithium.* Lithium, with a specific gravity of 0.534, is the lightest of all metals. It has two isotopes,  $\text{Li}^6$  and  $\text{Li}^7$ , of which  $\text{Li}^7$  is much more abundant. It is silvery white and softer than lead, but harder than sodium or potassium. Lithium salts give a crimson flame test. Lithium is very active chemically and combines readily with other elements. It is one of the alkali metals, others being sodium, potassium, rubidium, and cesium. Many of its compounds and chemical reactions, however, resemble those of the alkaline earth metals, beryllium, magnesium, calcium, strontium, barium, and radium.

Lithium when heated combines with most gases and is capable of absorbing even traces of them. In dry air at room temperature a protective coating of lithium nitride ( $\text{Li}_3\text{N}$ ) forms that prevents oxidation, but when heated to  $200^\circ \text{C.}$  it burns with an intense white light. At high temperature it combines with hydrogen to form lithium hydride ( $\text{LiH}$ ), a stable solid. Water decomposes lithium hydride, releasing hydrogen. One pound of lithium hydride reacted with water releases 40 cubic feet of hydrogen. With ammonia, lithium reacts to form lithium amide ( $\text{LiNH}_2$ ). Lithium combines with the halogens to form halides that resemble those of calcium more than those of sodium. All are soluble except for the fluoride, which, like fluorite ( $\text{CaF}_2$ ), is insoluble. Lithium chloride and bromide, like the calcium salts, are hygroscopic; that is, they readily absorb and retain moisture. Lithium bromide is one of the most hygroscopic compounds known.

If lithium is dropped into water, hydrogen gas is liberated and lithium hydroxide is formed, which is sparingly soluble. The reaction proceeds quietly, and, unlike that with sodium, insufficient heat is generated to ignite the hydrogen. Lithium hydroxide is usually prepared



from lithium ore minerals, and its principal use is in the manufacture of lithium grease.

Lithium carbonate, like calcium carbonate, is relatively insoluble; and it is decomposed by heat, but less readily than calcium carbonate. Lithium bicarbonate is an unstable compound. Lithium carbonate is used in greater quantity than any other lithium compound and is, in addition, the material from which lithium and most other lithium chemicals are made. Most of the phosphates of lithium are insoluble. Lithium sulfate is relatively soluble and resembles sodium sulfate rather than calcium sulfate in this respect.

*Uses.* Lithium metal is prepared on a commercial scale by the electrolytic reduction of a fused mixture of lithium chloride and other alkali salts. So far it is of limited usefulness, although in one method of manufacturing lithium hydride, lithium metal is reacted with hydrogen under high vacuum. Much of the lithium hydride produced is combined with ammonia to form lithium amide, which is an intermediate product in the manufacture of anti-histamines and other pharmaceuticals. Lithium metal is also used as a scavenger in refining nonferrous metals, and in the grain refinement of nodular iron in ferrous metallurgy. Lithium alloys of magnesium, aluminum, copper, lead, and zinc are under development and have promise. The most significant use of lithium may well be in connection with the hydrogen bomb. Although no information has been released, two applications for lithium have been postulated. In one, the lithium isotope  $\text{Li}^6$  is bombarded with neutrons in an atomic pile to produce tritium ( $\text{H}^3$ ) for use in the bomb; in the other, lithium plays an essential part in the thermonuclear reaction of the bomb itself.

It is in its compounds, however, that lithium has had its greatest application. The Edison alkaline storage battery, which contains lithium hydroxide, consumed the largest amount before World War II. During World War II the largest use of lithium compounds was for lithium hydride used as a source or carrier of hydrogen. Navy rescue kits contained small antenna balloons inflated with hydrogen obtained by adding sea water to lithium hydride. In addition, the armed forces required lubricants that were stable over a wide range of temperatures; and lithium stearate greases were developed that solved the problem. Since the war the use of lithium greases has expanded rapidly.

Today probably nearly half of the lithium compounds consumed in the United States are for lubricants; the ceramics industry accounts for an equal or slightly smaller amount; and less than 15 percent of the total is used for storage batteries, air conditioning, welding, organic synthesis, and miscellaneous purposes. In ceramics, lithium is used in special glasses, ceramic bodies, and glazes. Lithium is added in the form of lepidolite, spodumene, amblygonite, or petalite, or of frits prepared from lithium carbonate. Lithium-bearing frits have become accepted as standard materials for making porcelain enamels. The use of lithium-bearing eutectics permits lower firing temperatures and gives greater adherence of the enamel to the metal, higher gloss, and improved resistance to thermal shock.

Considering the small size of the production, a large number of applications for lithium have been proposed,

and some of them may become significant. Lithium chloride has been used in air conditioning for drying air, and lithium fluoride is employed in the welding and brazing of aluminum to dissolve aluminum oxide. Pyrotechnics require small amounts of lithium chemicals. Other applications include fungicides, the production of bleaching agents, lithium catalysts, lithium salt mixtures for heat transfer, cosmetics, and petroleum refining. A wider use of lithium chloride and lithium bromide for air conditioning has been predicted, and a second field where the applications of lithium may be expected to increase is organic synthesis.

*Markets and Prices.* Most lithium enters the market either as refined lithium chemicals or as lithium minerals that have been milled to specified grades. All of the major lithium producers in the United States, however, as well as some ceramic plants are potential buyers of clean, hand picked lithium minerals. Processing plants are located in South Dakota, Texas, North Carolina, New Jersey and Virginia.

Lithium materials are commonly sold on a contract basis. The American Potash & Chemical Corporation has announced that the following prices for contract tonnages will be in effect January 1, 1956:

Lithium carbonate, carload lots, 82 cents per pound, delivered.

Lithium hydroxide, carload lots, 80 cents per pound, delivered.

The prices paid for lithium minerals are not quoted in trade journals. According to Eigo and others (1955), prices received at the mine for spodumene, lepidolite, and petalite are \$11-\$12 per short ton unit of  $\text{Li}_2\text{O}$ , and for amblygonite, \$60-\$75 per short ton. Prices for lithium minerals are subject to negotiation; and the actual price received depends on the quality of the ore, the quantity to be shipped, and the distance from the deposit to the purchaser's plant.

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## MAGNESIUM AND MAGNESIUM COMPOUNDS

BY WILLIAM E. VER PLANCK

In California three plants produce magnesium compounds from sea water and sea-water bittern by treatment with calcined dolomite. A plant at Newark, Alameda County, and another at Moss Landing, Monterey County, produce magnesia refractories and specialty magnesias; and one at South San Francisco, San Mateo County, produces magnesium compounds of high purity for pharmaceutical and other uses. A fourth plant, at Chula Vista, San Diego County, produces magnesium chloride from bittern without the use of dolomite. In 1953 these plants produced 55,866 tons of magnesium oxide or its equivalent, valued at \$3,483,483. Not included in these figures is a very small tonnage of magnesite that was mined in the Red Mountain district, Santa Clara County.

Prior to 1945 magnesite deposits in California were worked on a large scale. They include, in addition to those in the Red Mountain district, deposits in the Porterville district, Tulare County; and the Bald Eagle mine, Stanislaus County. Until 1917 the only domestic production of magnesite came from California, and in World War I the California mines helped to relieve the critical shortage of refractory magnesite that developed when imports from Europe were cut off.

Magnesium metal has been produced in California by two thermal reduction plants, one at Permanente, San Mateo County, and the other at Manteca, San Joaquin County, that were built in World War II as part of a nation-wide program to supply the military demand for magnesium. Both were operated by the Henry J. Kaiser interests. The plant at Permanente operated from late 1941 until 1945 and has since been dismantled. The plant at Manteca operated from 1942 to 1944 and from 1951 until June 1, 1953. During the first period of operation it produced 22,368,900 pounds of magnesium ingots.

**Mineralogy and Geologic Occurrence.** Magnesium is a widespread element whose compounds are found in solution, in soluble salts derived from the evaporation of brines, in massive rocks, and in veins. In sea water it is the second most abundant metal after sodium. Sea water of average concentration contains the equivalent of 0.21 percent MgO which occurs as the chloride and sulfate.

Higher concentrations of magnesium occur in salt-works bittern, the tail liquor from solar salt works from which the carbonates, gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ), and most of the salt ( $\text{NaCl}$ ) have been precipitated by evaporation. The following analyses are of bittern produced at San Francisco Bay:

Component	Percent at 28° B $\phi$	Percent at 30° B $\phi$
NaCl	12.5	16.0
MgCl <sub>2</sub>	6.0	8.7
MgSO <sub>4</sub>	4.2	6.1
KCl	1.4	1.9
MgBr	0.14	0.20

Certain terrestrial brines are important sources of magnesium chemicals and, less commonly, of magnesia. The best known are the magnesium-calcium chloride brines of Michigan, Ohio, and West Virginia. In Cali-

fornia the brine of Bristol Lake, San Bernardino County, belongs to this class; but to date magnesium compounds have not been recovered from it.

**Soluble Minerals.** Magnesium salts are very soluble, and the most common ones are complex chlorides and sulfates with potassium or sodium. They include the following:

Carnallite	-----	$\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$
Langbeinite	-----	$\text{K}_2\text{SO}_4 \cdot 2\text{MgSO}_4$
Kainite	-----	$\text{KCl} \cdot \text{MgSO}_4 \cdot 3\text{H}_2\text{O}$
Bloedite	-----	$\text{MgSO}_4 \cdot \text{Na}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$
Epsomite	-----	$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$

Deposits of the potassium-bearing magnesium salts have not been found in California.

**Insoluble Minerals.** The most important insoluble magnesian ore minerals are magnesite ( $\text{MgCO}_3$ ) and dolomite [ $(\text{Ca}, \text{Mg})\text{CO}_3$ ]. Dolomite most commonly occurs as a sedimentary rock or its metamorphosed equivalent, dolomitic marble. Dolomite is discussed in another section of this bulletin. Brucite [ $\text{Mg}(\text{OH})_2$ ] and hydromagnesite ( $3\text{MgO} \cdot \text{Mg}(\text{OH})_2 \cdot 3\text{H}_2\text{O}$ ) are ore minerals at some localities but are not of commercial importance in California. The silicates olivine [ $(\text{Mg}, \text{Fe})_2\text{SiO}_4$ ], forsterite ( $\text{Mg}_2\text{SiO}_4$ ), and serpentine ( $\text{H}_4\text{Mg}_3\text{Si}_2\text{O}_9$ ) have minor uses as refractories and sources of magnesium compounds and may be important in the future.

Magnesite has three major geologic occurrences: (1) as replacement bodies in dolomite, (2) as fracture fillings and replacement bodies in serpentine, and (3) as sedimentary deposits associated with playa lake beds. The larger magnesite deposits of the world, including those of Chewelah, Washington, and Gabbs, Nevada, and those in Austria and Manchuria, are of the dolomite replacement type. The magnesite of these deposits is crystalline as contrasted with the cryptocrystalline or "amorphous" variety characteristic of deposits associated with serpentine and with lake sediments. In general, the ore bodies in dolomite are very large and comparatively impure, and the ore bodies associated with serpentine are small and comparatively pure. In general, the sedimentary deposits are small and impure.

**Localities.** Most of the magnesite deposits in California are associated with serpentine and occur in the Coast Ranges and in the western foothills of the Sierra Nevada. The largest known and most recently worked deposits are in the Red Mountain district on the border of Santa Clara and Stanislaus Counties and 30 miles southeast of Livermore. The Western mine, whose workings center about a group of veins that lie mainly on the Santa Clara County side of the line, has yielded approximately 870,000 tons of magnesite from 1905 to 1945. Since that time small quantities of magnesite sorted from the dumps have been shipped. Approximately 70,000 tons have been produced from the Red Mountain mine in Stanislaus County, which was active from 1915 to 1941. Still smaller tonnages were obtained from other deposits.

Probably second in total output is the Bald Eagle mine in Stanislaus County near the Merced County





FIGURE 1. Map of California showing location of magnesite deposits and plants producing magnesium and magnesium compounds.



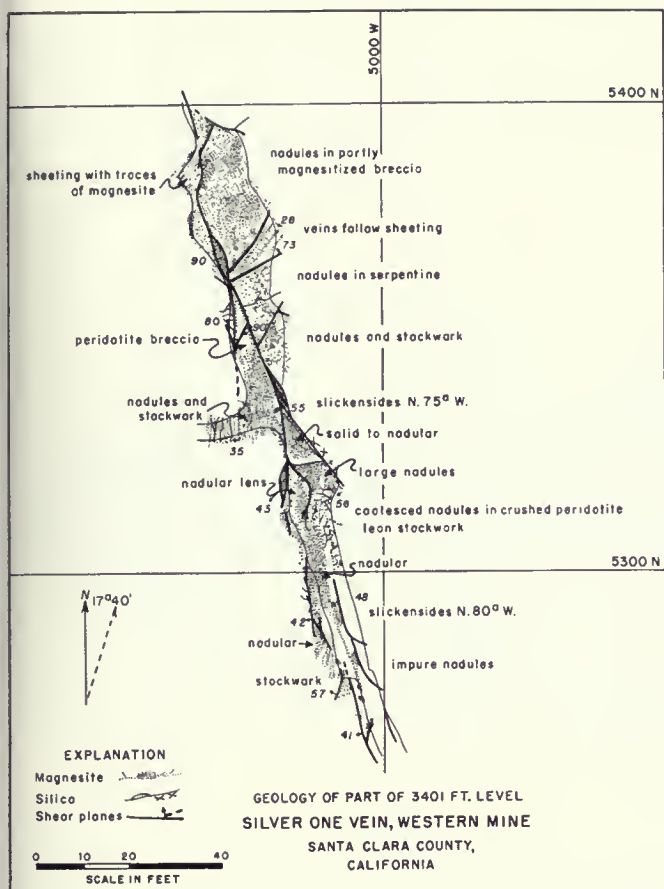


FIGURE 2. Geologic map of part of 3401-foot level, Silver One vein, Western mine, Santa Clara County, showing magnesite in a strong shear and breccia zone. After Bodenlos, 1950.

line and 20 miles southwest of Gustine. Large-scale operations began in 1930, and the mine was closed in 1944.

Mines of the Porterville district east of Porterville, Lindsay, and Exeter in Tulare County furnished most of the magnesite mined in California prior to 1930. The total production of the Porterville district is probably about 500,000 tons. Other mines that yielded substantial tonnages of magnesite in the 1920s and earlier were the Sampson mine in San Benito County and near the New Idria quicksilver mine; the Snowflake and Blanco mines in Chiles Valley, and the White Rock mine in Pope Valley, all in Napa County; a mine on Austin Creek north of Cazadero, Sonoma County; and a mine on Cedar Mountain in Alameda County 11 miles southeast of Livermore. Additional magnesite deposits that are associated with serpentine have been worked in Mendocino, Kings, Placer, Fresno, Tuolumne, and Riverside Counties.

The Red Mountain magnesite deposits, which have been studied in detail by Bodenlos (1950), are generally typical of all the deposits enumerated above except the Bald Eagle deposit. The deposits at Red Mountain have formed in a large sill-like, ultrabasic intrusive body and occur as replacements of serpentine in shear zones and tension fractures and locally as fissure fillings. The magnesite is characteristically white, porcelain-like, and cryptocrystalline. Opal, chalcedony, calcite, and the hy-

drous magnesium silicates deweylite and sepiolite form veinlets that cut the magnesite. Minor proportions of dolomite, manganese oxide, and unreplaced serpentine occur in the ore also. Portions of some veins are as much as 30 feet thick, but most of the ore shoots mined in 1944 were 5 to 10 feet wide. When the mine was in operation, veins narrower than 2 or 3 feet could not be profitably worked. Ore shoots are rarely more than 500 feet in length and depth. Mineralization has been observed through a vertical range of 500 to 700 feet and may extend much deeper. Magnesite associated with serpentine is believed to be an alteration product resulting from the action of aqueous solutions rich in carbon dioxide on magnesium silicates. Though descending groundwater has been postulated as the mineralizing agency, Bodenlos (1950, pp. 259-266) presents evidence that the waters that produced the Red Mountain deposits were hydrothermal.

At the Bald Eagle mine the magnesite also has replaced serpentine. The principal deposit is moderately dipping and tabular in shape, and it occurs near the base of a body of brecciated serpentine that is underlain by Franciscan sedimentary rocks. The breccia may be an old slide. The magnesite is locally as much as 30 feet thick, but averaged about 4 feet in thickness.

*Deposits Associated With Dolomite.* Some small magnesite bodies that have replaced dolomite occur near Barstow (Bowen, 1954, pp. 170, 171) and Mountain Pass (Rubey, 1936, pp. 118-119), San Bernardino County; and there may well be others in the state. This magnesite is cryptocrystalline, not crystalline.

*Sedimentary Deposits.* Sedimentary magnesite has been mined at Bissell, Kern County (Gale, 1912, pp. 512-516); and similar deposits occur near Afton (Rubey, 1936, pp. 117, 118), Needles (Vitaliano, 1950), and in the Kramer Hills (Bowen, 1954, pp. 171, 172), San Bernardino County. The deposits are small, and with the exception of the Needles deposit, comparatively impure. The magnesite, which is cryptocrystalline but soft and chalky, is interbedded with folded playa lake sediments of Tertiary age. The deposits are believed to have precipitated from saline lake water and should perhaps be considered as saline deposits.

*Deposits of Soluble Magnesium Minerals.* Attempts have been made to mine epsomite from a point in San Bernardino County 20 miles east of Searles Lake and west of the Owlshhead Mountains where efflorescent salts occur on the outcrops of Tertiary clay beds. The American Magnesium Company was active there from 1922 to 1926 and shipped some material over a monorail constructed through Wingate Pass to a station on the Trona Railroad south of Searles Lake. Bloedite ( $\text{MgSO}_4 \cdot \text{Na}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$ ) is present in a sodium sulfate deposit in the Durmid Hills, Imperial County.

*Mining Methods.* Most of the narrow, steeply dipping magnesite veins associated with serpentine have been mined by underground methods, although the outcrops of some veins were mined with open cuts. Open stoping, modified shrinkage stoping, and cut-and-fill stoping have been employed. To obtain ore of shipping grade, careful mining to avoid dilution was necessary;





FIGURE 3. Photo showing magnesite plant of Kaiser Aluminum & Chemical Corporation, Moss Landing, Monterey County.

and often the magnesite was hand sorted in the stopes. In some places ore was left to support weak walls.

*Moss Landing Plant.* The magnesite plant of Kaiser Aluminum & Chemical Corporation is at Moss Landing, Monterey County. Raw materials are sea water, pumped from nearby Elkhorn Slough at the rate of 30 million cubic feet per day, and caustic calcined dolomite prepared at the Natividad quarry, 12 miles away by road.

In the first step, the calcined dolomite is formed into a slurry with water. Lumps of calcined dolomite quickly disintegrate, while almost all of the impurities present in the dolomite settle and are removed by classification. Next the raw sea water is treated with a portion of the calcined dolomite slurry in order to precipitate dissolved carbon dioxide as calcium carbonate. The operation is carried out in three pre-treatment tanks operated in parallel. The carbon dioxide-free water then goes to the reaction tank where the rest of the calcined dolomite slurry is added. The calcium of the dolomite is replaced by magnesium in the sea water. Magnesium, which originates from both the dolomite and the sea water in approximately equal proportions, precipitates as the hydroxide. The physical properties of the precipitate, particularly its filtering characteristics, depend in large measure on the conditions maintained in the reaction tank. The magnesium hydroxide precipitate is thickened in two 250-foot thickeners. The overflow is returned to the sea, and the underflow is washed free of chlorides with fresh water in two additional 250-foot thickeners. The washed magnesium hydroxide is dewatered with Oliver filters. Some filter cake is marketed without further treatment; but most of it is calcined. Calcination is carried out in two Schmidt kilns of the type used in

portland cement plants. Dust collected from the kilns is added to the filter cake and recalcined. By the addition of small quantities of iron, silica, and other materials, and by varying the temperature of the kiln a number of different magnesias are made. Still more products are produced by blending. Magnesite that contains a few percent of silica is called periclase.

A portion of the periclase is consumed in an adjoining refractory brick plant where periclase-chrome brick of several compositions are manufactured. Most of the chromite is obtained from the Philippine Islands, but some comes from California. Periclase and chromite are crushed, weighed out, and mixed with a small amount of water. Brick are shaped with hydraulic presses and stacked on pallets for handling. Burning is done in a continuous kiln equipped with automatic combustion controls. For chemically bonded brick, which are not burned, a chromium chemical is added.

*The Manteca Plant* (Schrier, 1952). The United States Government's silicothermic magnesium plant is 2 miles west of Manteca, San Joaquin County. The plant was reactivated in February 1951 and operated by Kaiser Magnesium Company. Production began June 6, 1951, and continued until June 1, 1953, when the plant was again placed on a standby basis. It has since been leased by Western Pyromet Company which has announced plans to produce titanium.

In the silicothermic or ferrosilicon process calcined dolomite is reduced with silicon in the form of ferrosilicon at high temperature in a highly evacuated retort. Magnesium vapor is liberated and condenses in the water-cooled outer end of the retort which projects out of the furnace. The calcium oxide of the dolomite com-



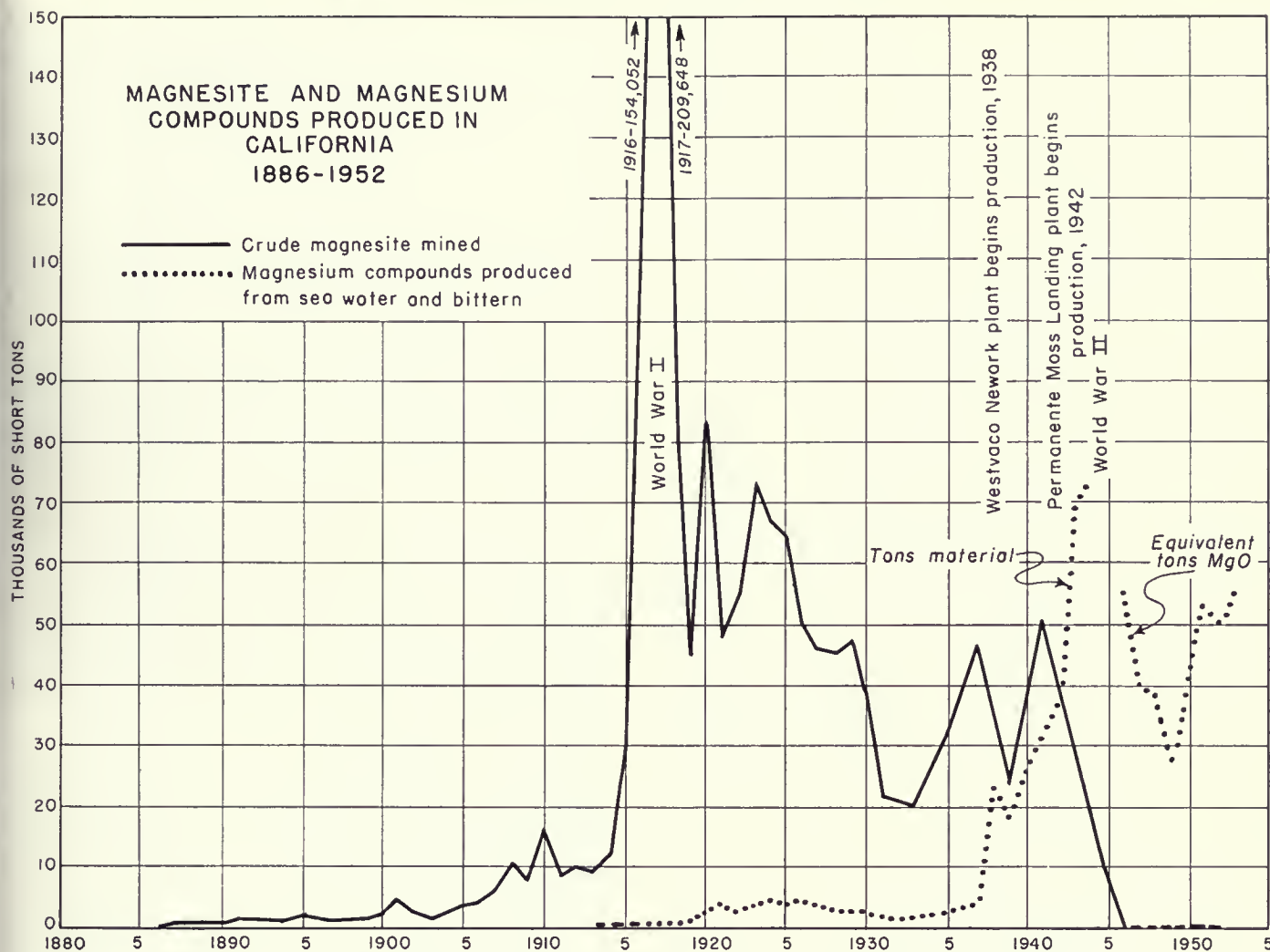


FIGURE 4. Chart showing production of magnesite in California, 1886-1953, and of magnesium compounds produced from sea water and bittern in California, 1916-53.

bines with the oxidized silicon and prevents the formation of magnesium silicates, which are difficult to reduce. Pure magnesium oxide cannot be reduced by the silicothermic process. The iron of the ferrosilicon plays no part in the reduction. The charge contains, in addition, a small amount of fluorite, which in some manner not fully understood increases the yield.

In normal times magnesium is reduced by the electrolysis of a mixture of fused magnesium and other chlorides, and the silicothermic process is not competitive. The large amount of hand labor required, the cost and short life of the retorts, and the complex vacuum system contribute to its high cost of operation. Its advantages are that plants using it can be built quickly, the principal raw materials are seldom in short supply, and it does not consume large quantities of electricity.

The Manteca plant employed hard-burned dolomite from the Kaiser plant at Natividad, 75 percent ferrosilicon from the Kaiser plant at Permanente, and acid-grade fluorspar from Zuni, New Mexico. Dolomite was ground to 80 percent minus 100 mesh and ferrosilicon to 70 percent minus 200 mesh at the Manteca plant and then mixed with fluorspar in an automatic batching

plant. The mixture contained 4.5 parts of dolomite, 1 part of ferrosilicon, and 2.5 percent by weight of fluorspar. Briquette machines compressed the powder into walnut-sized pellets without binder, and the pellets were placed in paper bags, 40 to 50 pounds per bag, for charging into the retorts.

The plant contained 64 gas-fired furnaces, each with 16 horizontal retorts or a total of 1024 retorts. The retorts, which were cast of a special nickel-chromium alloy steel, were 10½ feet long by 10 inches in diameter. They projected approximately 2 feet outside the furnace, and this portion was cooled with a water jacket. Each was equipped with a 1½-foot sleeve that fitted loosely within the water-cooled section and served to collect the condensed magnesium vapor. A double-layered plug that fitted into the end of the sleeve collected any alkali metal liberated. By means of an eye in the alkali-metal collector, the sleeve with its magnesium crystals could be withdrawn from the retort. A loosely fitting metal heat dam placed 2 feet from the mouth protected the sleeve from radiant heat. The retorts were closed with covers fitted with rubber gaskets. Two vacuum systems served the retorts, a low vacuum system provided with a



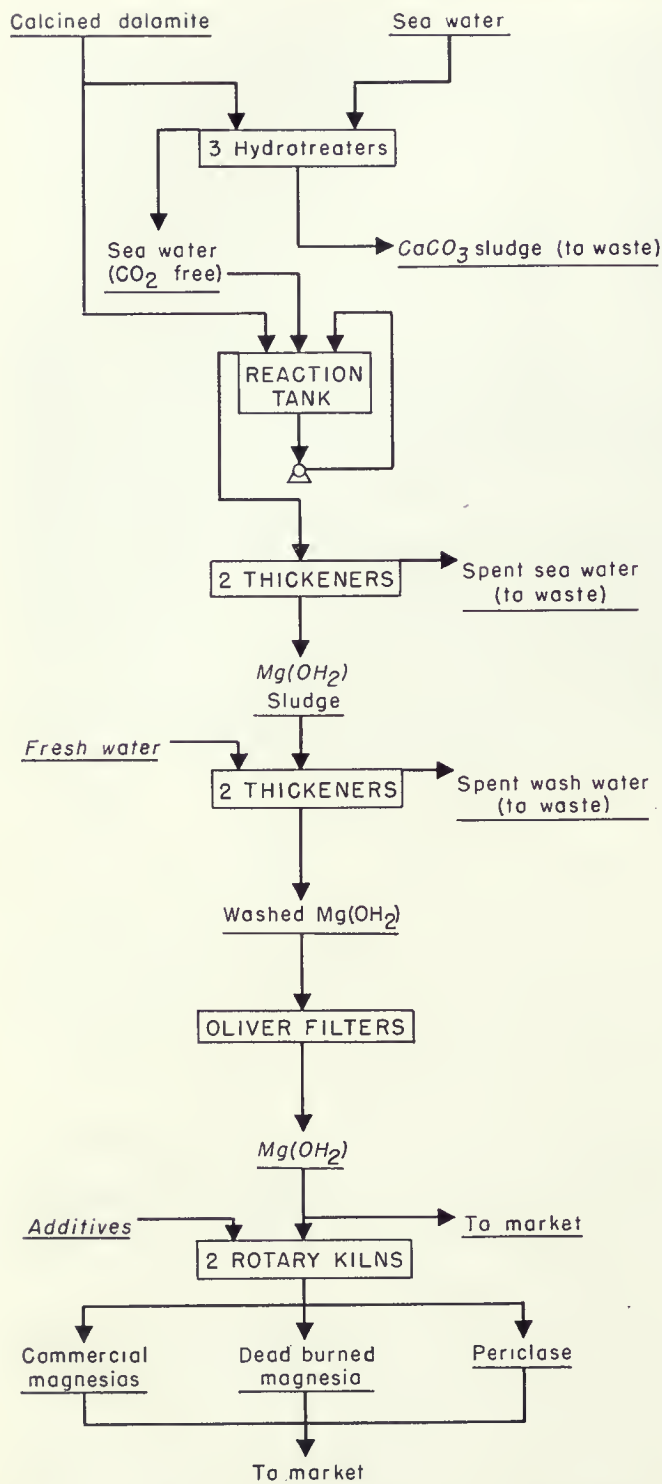


FIGURE 5. Flow sheet of Moss Landing plant, Kaiser Aluminum & Chemical Corporation, Monterey County.

single large pump of the reciprocating type, and a high vacuum system that contained both Stokes and Kinney pumps. One pump was provided for every four retorts, and all pumps were served by a common oil supply and reconditioning system.

The retorts were charged and unloaded in the following manner. Each retort, which was kept continuously

at a temperature of 2140° F, was charged by hand with five bags of pellets and left open for about 15 minutes while the paper burned away and most of the moisture was driven off. Then the heat dam and the sleeve with its alkali-metal collector were inserted, the retort was closed and placed on low vacuum, 26 inches of mercury, for 30 minutes while the remaining moisture and volatiles were drawn off. By means of the second system the vacuum was increased to 100 to 150 microns of mercury and maintained for 9 hours. Magnesium condensed as a "muff" of coarse crystals on the inside of the sleeve. About 35 pounds of magnesium were recovered from each retort charge.

After the retort was unsealed the sleeve was withdrawn. Any alkali metal present in the collector ignited upon contact with the air. If more than 0.1 percent alkali metal was present in the magnesium, the entire muff ignited and could be extinguished only with great difficulty. The muff was forced from the sleeve with a hydraulic press and carried to the foundry for remelting. Residue, still in pellet form, was hand-shoveled from the retort, and the retort was reloaded at once.

Under the influence of the high temperature and vacuum, the retorts occasionally collapsed. They were inflated with compressed air while in the hot furnace and could be restored several times in this way before cracks developed. Retorts were taken out for scrapping and replaced with new ones without shutting down the furnace.

At the foundry the muffs were remelted with Dow 230 flux in gas-fired steel pots. The pure magnesium was then hand-ladled from the pots and cast into 17-pound ingots in molds mounted on a conveyor. The magnesium produced was Grade B and met specification P-71 which calls for 99.8 percent magnesium, less than 0.02 percent copper, 0.005 iron, and 0.001 percent nickel. Magnesium ingots can be stored in the open if circulation is present to keep them dry. Inclusions of magnesium oxide, especially in the presence of moisture, are centers of disintegration.

Sludge from the melting pots was processed for the recovery of flux and magnesium metal.

Residue from the retorts consisted of dicalcium silicate and iron oxide with some magnesia, free lime, and fluorine. Although the composition is somewhat similar to that of portland cement, no use has been found for it.

*The South San Francisco Plant.* The plant of Marine Magnesium Products Division of Merck and Company, Inc., is at South San Francisco, San Mateo County. Originally called the Marine Chemical Company, this organization has been producing high-purity magnesium compounds since 1928. Relatively small quantities of high-priced products are made, and raw materials of high purity are consumed. Raw materials are calcined dolomite and sea water taken from San Francisco Bay near the plant. Normally the bay water contains the equivalent of roughly 2 grams of magnesium oxide per liter. When the Sacramento River is in flood, however, the water is materially diluted; and the plant feed is enriched with salt-works bittern.

The first step is the preparation of the water. Organic matter is killed with chlorine gas, and dissolved calcium carbonate is precipitated with a small quantity of cal-



cined dolomite. Next the treated water is filtered, and magnesium hydroxide is precipitated by the addition of a larger quantity of calcined dolomite. The precipitate is a gummy slime that requires special and elaborate handling for the removal of sodium and displaced calcium salts and for dewatering. Depending on the product desired, the magnesium hydroxide is dried, carbonated, or calcined.

**The Chula Vista Plant.** The plant of Westvaco Chemical Division, Food Machinery and Chemical Corporation at Chula Vista, San Diego County, produces magnesium chloride. Much of the output is used for magnesium oxychloride cement. Bittern, the principal raw material, is obtained from the adjoining solar salt plant of the Western Salt Company and further evaporated by the use of heat. Salt and carnallite ( $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ) that crystallize are discarded, and magnesium chloride is obtained by concentrating the residual liquor.

**The Newark Plant.** Westvaco Chemical Division, Food Machinery and Chemical Corporation produces magnesia, bromine, and gypsum from bittern in a large plant at Newark, Alameda County. Bittern is obtained from the Leslie Salt Co. during the short salt harvesting season and stored in ponds large enough to hold a year's supply. Bromine is recovered from the bittern before further processing. The bromine operation, which is described elsewhere in this bulletin, has no effect on the recovery of magnesia.

An essential preliminary step, however, is the removal of sulfate, which is accomplished by the addition of calcium chloride-rich end liquor. The reaction is carried out in Pachuca tanks. The gypsum that precipitates is removed with Dorr thickeners and dried. It is a product of high purity that finds a ready market as a retarder for portland cement and in agriculture.

The sulfate-free overflow from the Dorr thickeners, which is essentially magnesium and sodium chloride, is reacted with calcined dolomite. Conditions are maintained that cause a granular precipitate of magnesium hydroxide to form. Thickening and washing are carried out in a series of five Dorr thickeners. Depending on the product desired, silica, alumina, iron oxide, or lime is added, and the hydroxide is calcined in rotary kilns. Approximately half of the output is periclase, a refractory magnesia prepared at high temperature; the remaining products are various grades of caustic calcined magnesia. Dolomite is obtained from the company's quarry near Hollister, San Benito County, and calcined at Newark.

**Uses.** Magnesium metal is used mostly in the form of high-magnesium alloys as a lightweight structural material. The largest application is for military aircraft, and non-military applications are still in the development stage. Nevertheless, significant amounts are used for paper-mill rolls, portable tools, ladders, hand trucks, portable ramps, and parts of calculating machines where light weight is essential. Structural products consumed 27,742 tons of primary magnesium in 1952. Non-structural uses, which consumed 16,105 tons, include aluminum and other alloys, the cathodic protection of pipe-

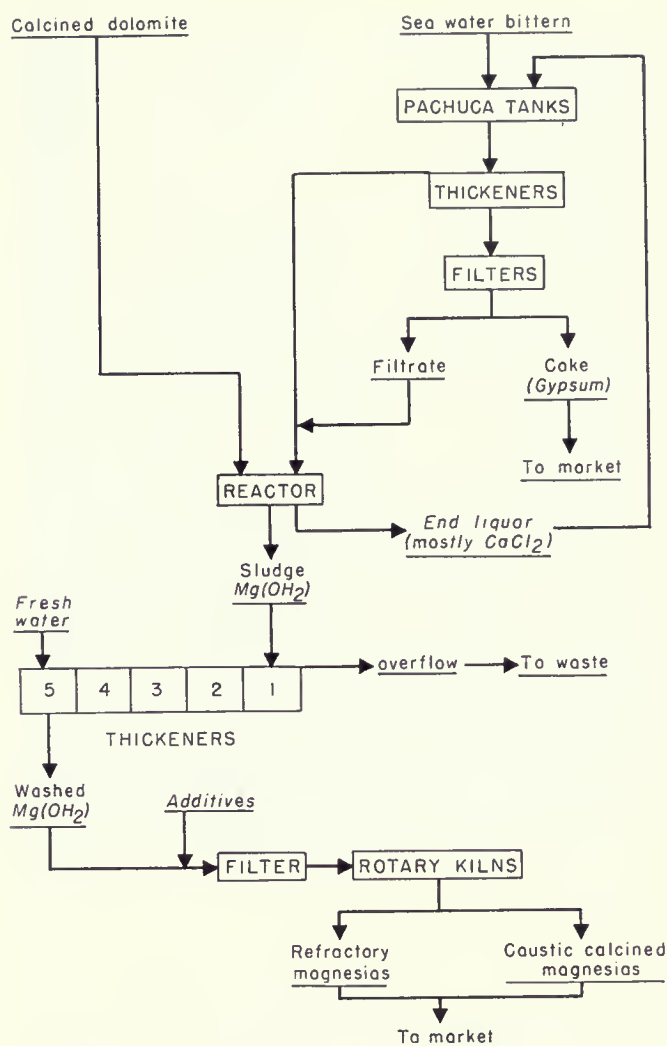


FIGURE 6. Flow sheet of Newark plant, Westvaco Chemical Division, Alameda County.

lines, chemical uses, scavenging and deoxidizing in metallurgy, and the reduction of titanium.

Magnesium oxide is one of the principal basic refractories used for lining high-temperature furnaces and kilns. The oxide as well as other magnesium compounds have, in addition, numerous other industrial applications such as for thermal insulation, in magnesium oxychloride cement, and in the manufacture of rubber and rayon. About 85 percent of the magnesium compounds produced in the United States is marketed for refractory purposes.

The terminology of the magnesium oxide compounds is confused. Magnesite in a strict sense is natural magnesium carbonate ( $\text{MgCO}_3$ ) and magnesia is magnesium oxide ( $\text{MgO}$ ). Natural magnesia is the mineral periclase. Calcined magnesite is roughly synonymous with magnesia because by heating, magnesite is dissociated into magnesia and carbon dioxide ( $\text{MgCO}_3 + \text{heat} \rightarrow \text{MgO} + \text{CO}_2$ ). In practice the term "calcined" is often dropped, and the term magnesite commonly means magnesia obtained by the calcination of the mineral magnesite or of some other magnesium compound such as the natural or synthetic hydroxide [ $\text{Mg}(\text{OH})_2$ ].





FIGURE 7. Photo showing press for forming refractory brick, Kaiser Aluminum & Chemical Corporation, Moss Landing, Monterey County.

The chemical and physical properties of the commercial magnesias are greatly influenced by the temperature of calcination. Magnesias fall into two classes, dead-burned magnesite and caustic calcined magnesite. Dead-burned magnesites are produced by calcining magnesium carbonate or magnesium hydroxide at temperatures of  $1560^{\circ}\text{C}$  or higher. They are chemically inert and contain from 2 percent to less than 0.5 percent carbon dioxide. They contain various proportions up to 15 percent of iron oxide, silica, alumina, and lime present as impurities in the raw material or added to the kiln charge. These materials act as fluxes and produce a sintered, granular product. Periclase is the name given to a dense crystalline magnesia containing over 90 percent  $\text{MgO}$  with silica as the principal additive. It is obtained by calcination at about  $1760^{\circ}\text{C}$ , and today most periclase is made from synthetic magnesium hydroxide.

The dead-burned magnesites are used for refractory purposes. Grain magnesite is a granular material composed of iron-bearing, dead-burned magnesite that is used for the construction and maintenance of furnace bottoms. Basic refractory brick for furnace walls are made from dead-burned magnesites, especially periclase, and chromite. The steel industry consumes about 5 pounds of refractory magnesia for each ton of steel produced. Other large consumers of magnesia refractories are portland cement plants, copper and lead smelters, and the magnesia calcining plants themselves.

Caustic calcined magnesite is produced by calcining magnesium carbonate or magnesium hydroxide at temperatures of  $1200^{\circ}\text{C}$  or less. It contains up to 97 percent magnesium oxide and 1 to 5 percent of carbon dioxide or combined water. Like calcium oxide, it is chemically active and slakes in water and air. Iron oxide, silica, alumina, and lime are undesirable diluents.

Caustic calcined magnesite has broad applications, and commonly products of particular compositions and properties are produced for the use of specific consumers. One of the oldest uses is in magnesium oxychloride cement. Finely ground caustic calcined magnesite mixed with a 20 percent solution of magnesium chloride sets in 3 to 4 hours. The product is hard and strong, can be cut and polished, and can receive nails or screws. Usually sand, sawdust, or other filler is added. The composition is thought to be  $3\text{MgO}\cdot\text{MgCl}_2\cdot 7\text{H}_2\text{O}$ . Today its largest application is for ship decks and floors of railroad cars.

Caustic calcined magnesite also is used in the manufacture of rayon, as an active ingredient in rubber, and as an adsorbent. The historic magnesium bisulfite process for producing pulp for paper has been revived, because, in contrast with the calcium bisulfite process, the waste liquor can be disposed of comparatively easily.

Other magnesium compounds that have commercial uses include the hydroxide, chloride, sulfate, and carbonate. In California magnesium hydroxide is the raw material for manufacturing basic magnesium carbonate, but elsewhere in the United States it is made from dolomite. Basic magnesium carbonate is a fluffy material that is used for thermal insulation. Its chemical formula has not been determined, but one that has been proposed is that of the mineral hydromagnesite  $[3\text{MgO}\cdot\text{Mg}(\text{OH})_2\cdot 3\text{H}_2\text{O}]$ . In addition, small quantities of magnesium hydroxide are used as pharmaceuticals.

Magnesium chloride is used in the manufacture of magnesium oxychloride cement, as a ceramic raw material, and for the sizing of paper. Magnesium metal is produced from it by electrolysis.

Magnesium sulfate is a fireproofing and sizing agent. Epsom salt is the hydrate  $\text{MgSO}_4\cdot 7\text{H}_2\text{O}$ .

Magnesite is still the world's principal source of magnesia, although none has been produced in California for that purpose since 1945. Almost all magnesite is calcined before use. Uncalcined, it is one of several raw materials that are used for producing magnesium sulfate and magnesium chloride.

**Marketing.** Almost all the dead-burned and caustic calcined magnesite produced in the United States is manufactured by about six companies that have developed equipment and techniques for producing magnesia on a large scale. Much of the refractory magnesia produced in California is marketed in the east, although with the expansion of the steel and portland cement industries in the west, California magnesia producers are becoming less dependent on eastern markets. California producers specialize in high-purity products such as periclase that are better able to carry transportation charges than such products as grain magnesite.

Present conditions do not favor the mining of magnesite in California. Manufacturers of magnesia in this state no longer use natural magnesite because of its vari-



able composition compared with sea-water magnesia, the distance of the deposits from markets, and increased costs of mining. The steeply dipping, narrow, discontinuous ore bodies typical of the California deposits are not amenable to low cost, mechanized mining methods. Probably all of the known developed reserves were approaching exhaustion when large-scale mining ceased.

Certain plants in California that produce magnesium chemicals still consume a few hundred tons per year of magnesite from the Red Mountain district. Because of its purity, freedom from traces of objectionable elements, and certain physical properties, no feasible substitute has been found.

Magnesite mined by Westvaco Chemical Division and its predecessors from the Western mine and the Bald Eagle mine averaged about 95 percent  $\text{MgCO}_3$ , 2 percent  $\text{CaCO}_3$ , and 3 percent silica. By simple methods of beneficiation silica could be reduced to less than 1 percent. A typical analysis of beneficiated magnesite from Chewelah, Washington, follows (Harness 1943, p. 7):

Component	Percent
MgO -----	42.5
SiO <sub>2</sub> -----	4.2
Fe <sub>2</sub> O <sub>3</sub> -----	0.96
Al <sub>2</sub> O <sub>3</sub> -----	0.41
CaO -----	2.76
H <sub>2</sub> O -----	0.06
CO <sub>2</sub> -----	48.6

**Prices.** In 1957 the price of magnesium metal was about 36 cents per pound. Dead-burned grain magnesite in bulk cost \$40.00 per ton f.o.b. Chewelah, Washington. The price of kiln-run 90 percent periclase was \$57.00 per ton in bulk, f.o.b. Newark, California; and the price of powdered caustic calcined magnesia, oxychloride cement grade, was \$75.00 per ton in bags, f.o.b., Newark, California. Prices for uncalcined magnesite are not published.

**History of the California Magnesia Industry.** The history of the magnesia industry in California is the development of three separate industries that produce similar products from different raw materials. In the first, magnesite is the raw material; in the second, bittern; and in the third, sea water. The magnesite industry and the bittern industry originated in the late 19th century as unrelated industries that were coordinated and merged by predecessors of Westvaco Chemical Division during the 1930s and 1940s. The sea-water industry was developed by Henry J. Kaiser during World War II.

**Magnesite.** The magnesite near Porterville was observed and described by W. P. Blake in 1853, but the first recorded production was from Cedar Mountain, Alameda County, in 1886. Ore was first shipped from the Snowflake mine, Napa County, in 1891, and from the White Rock mine, Napa County, in 1894. The Red Mountain district was opened in 1899, and the Harker mine near Porterville was first worked in 1900. These operations were small, and production in the 10 years prior to 1915 totaled just under 80,000 tons. In those days the United States was dependent upon Europe for refractory magnesite, and much of the California magnesite was consumed at the plant of the Western Carbonic Acid Gas Company in the area now occupied by Emeryville. At this plant caustic calcined magnesite was produced

in a shaft kiln and shipped to pulp mills in Oregon that used the magnesium bisulfite process. The carbon dioxide evolved was marketed in liquid form. In addition, a magnesite brick plant was in operation in the Bay area in 1905.

Around 1910, cheaper sources of carbon dioxide were developed, although the paper industry remained an important market for magnesia. In this period the use of magnesium oxychloride cement, invented in France, was growing and was consuming increasing quantities of California magnesite.

With the outbreak of war in Europe in 1914 and the cutting off of Austrian magnesite, steel makers turned in desperation to California, the only domestic source of magnesite. The few producers of magnesite in California were in no position to supply the demand, and there followed a wild scramble to reopen dormant mines and develop new deposits. A record of 209,648 tons was produced in 1917. The California product was expensive because of the distance to the eastern steel mills. Moreover the quality was poor because few people understood the requirements of good refractory magnesia, the effects of silica, iron, and lime in the ore, or the proper calcination conditions. The market vanished before these problems were fully solved. Shipments of magnesite from the Chewelah area in Washington, which closely resembles that from Austria, began in 1916; and with the resumption of imports when peace was declared, California was left with only a local market for refractory magnesite. For perhaps 20 years most of the California magnesite was used in the manufacture of oxychloride cement, for which it is particularly suited.

The seeds of the modern California magnesite industry were sown in World War I, however, particularly in the Porterville district, which had yielded more than half the magnesite mined during the war. In 1920 the National Kellestone Company, a large manufacturer of oxychloride cement, organized the Sierra Magnesite Company to furnish its requirements of caustic calcined magnesite. The largest deposits and plants in the Porterville district were acquired. A method of beneficiating crude magnesite by screening out silica-rich fines was developed, the rotary kiln was adapted, calcining techniques and methods of control were worked out, and for the first time artificial periclase was produced from magnesite in the rotary kiln. Previously periclase had been prepared by the fusion of dead-burned magnesite in the electric furnace.

In addition to the Sierra Magnesite Company, a few other companies produced magnesite in California after World War I. C. S. Maltby Company Ltd. operated the Western mine from 1919 to 1931, the Snowflake and Blanco mines in 1923 and 1924, and the Sampson Peak mine from 1923 to 1926. The California Magnesite Company worked the Harker mine from 1923 to 1926, and the California Magnesite Company operated the Red Mountain mine intermittently between 1922 and 1932. In 1941 the Magnesite Products Company worked the Red Mountain mine and the Gray Eagle mine, Tuolumne County, on a small scale.

The Sierra Magnesite Company acquired the Bald Eagle mine to replace the depleted deposits at Porterville which were last worked in 1931. Production from the new mine began in 1930. In 1932 the Western mine



and other properties in the Red Mountain district were leased. In 1934 the Sierra Magnesite Company and the California Chemical Corporation, another subsidiary of the National Kellestone Company, were merged to form the California Chemical Company; and early in 1937 the latter passed into the hands of Westvaco Chlorine Products Corporation. Despite the increasing importance of bittern as a source of magnesium compounds that these changes of name imply, magnesite was consumed in large amounts through World War II. Westvaco Chlorine Products Corporation and Kaiser interests formed a new Sierra Magnesite Company in 1941 to work deposits of magnesite and brucite near Luning, Nevada. Ore from this operation replaced that from the Bald Eagle mine, which was worked out in 1944. As already mentioned, the Western mine was virtually closed in 1945. Westvaco relinquished the lease on the property about 1953, and the Nevada operation also has been closed.

**Bittern.** The large-scale recovery of magnesium compounds from bittern has developed within the past 25 years. In 1880, however, the Union Pacific Salt Company was producing magnesium carbonate at the rate of 50,000 pounds per year by carbonating bittern near Alvarado. The product was used by the Hercules Powder Company as an absorbent in the manufacture of dynamite. The manufacture of oxychloride cement created a market for magnesium chloride, and at least some of it was obtained at San Diego Bay prior to the failure of the Otay dam in 1916. The resulting flood destroyed both the magnesium chloride plant and the salt works. Although the salt works was rebuilt, bittern salts were not produced for a number of years.

The shortage of chemicals during World War I created a new interest in bittern, and several plants were built that employed a process similar to that now used by Westvaco Chemical Division at Chula Vista. Most of the plants produced magnesium chloride in either liquid or solid form, and a few of them recovered magnesium sulfate and potassium chloride also. Production by the Oliver Salt Company at Mount Eden, Alameda County, and the Marine Chemical Company at Long Beach, Los Angeles County, began in 1916. The Whitney Chemical Company, a subsidiary of the Leslie Salt Refining Company at San Mateo, followed in 1917; and in 1919 the California Chemical Company began production at Chula Vista, San Diego County.

The National Kellestone Company, whose subsidiary the Sierra Magnesite Company, was successfully operating at Porterville, decided to enter the magnesium chloride field. A second subsidiary, the California Chemical Corporation, was organized in 1923, and the plant of the California Chemical Company at Chula Vista was purchased. A much larger plant was built and is still in operation. The management of the California Chemical Company then built another plant at Newark, Alameda County, and operated it under the name of the Industrial Chemical Corporation until 1927.

After World War I, when magnesium chloride from Germany was available again, the California plants operated at a disadvantage. By 1928 all but the California Chemical Corporation's plant at Chula Vista had been closed. Then the California Chemical Corporation arranged long-term contracts for bittern with the

salt companies on San Francisco Bay and purchased the small plant of the Industrial Chemical Corporation at Newark.

Because the market for magnesium chloride was limited, research was initiated on the problem of recovering additional magnesium compounds from bittern. The precipitation of magnesium hydroxide from bittern and the calcination of San Francisco Bay shells to form the lime required were studied at Porterville. The calcination of shells was further studied in a small plant at Newark that began the commercial production of lime in the fall of 1930. A pilot plant was then built at Newark in which magnesium hydroxide precipitated from bittern with lime could be carbonated to make basic magnesium carbonate or calcined to make magnesia. In February 1937, soon after the operation was acquired by Westvaco Chlorine Products Corporation, construction began on the plant at Newark, which is still in operation. The production of magnesia from precipitated magnesium hydroxide brought a host of new problems, and natural magnesite was used for some purposes until about 1951. Calcined dolomite was substituted for shells as the precipitating agent in 1947. In 1948 the Westvaco Chlorine Products Corporation became the Westvaco Chemical Division, Food Machinery & Chemical Corporation.

The Plant Rubber and Asbestos Company at Redwood City, San Mateo County, also produced magnesia from bittern between 1933 and 1941. In this operation magnesium hydroxide was precipitated with crude soda ash made by calcining trona and converted to basic magnesium carbonate. After the salt plant from which the bittern came was closed, Plant Rubber and Asbestos Company purchased magnesium hydroxide.

**Sea Water.** The world's first commercial production of magnesium compounds from sea water was obtained in 1928 at South San Francisco. Relatively small amounts of high priced compounds such as milk of magnesia were produced by the Marine Chemical Company, which since 1951 has been the Marine Magnesium Products Division of Merck & Company, Incorporated. The Henry J. Kaiser interests, which now operate the much larger Moss Landing plant, entered the magnesia field by way of the magnesium metal industry.

In the period from 1939 to 1941, when war was imminent, the anticipated military demand for magnesium was far above existing plant capacities. In order to increase production, the Federal Government first encouraged private industry by helping to finance new construction. In California, Henry J. Kaiser interests formed the Permanente Metals Corporation and built a thermal magnesium reduction plant at Permanente in 1941. Production began late the same year, although the output remained small throughout 1942. The Government then built 13 additional plants that used various processes, and all but one were brought into production during 1942. One of these plants was at Manteca, San Joaquin County; and it was operated for the Government by Permanente Metals Corporation.

The plant at Permanente, which was the only one of its kind in the United States, employed a modified Hansgirg carbothermic process. A mixture of magnesia and finely divided carbon was fed into an arc furnace where the magnesia was reduced to magnesium vapor.



This hot vapor tended to reoxidize explosively; but by shock cooling in a reducing gas, a large part of it could be recovered as magnesium dust. The original Hansgird process employed hydrogen, but the Permanente plant employed the natural gas that was required for firing the kilns of the adjacent portland cement plant. The magnesium dust was either used to fill large incendiary bombs or briquetted and distilled to produce magnesium ingots.

It had been contemplated that the magnesia required at Permanente would be produced from magnesite. As already related, Kaiser and Westvaco interests formed the Sierra Magnesite Company in 1941 to mine brucite and magnesite in Nevada. Permanente Metals Corporation produced dead-burned magnesite at San Jose in 1942 and 1943, but much if not all of the magnesia used initially at Permanente was produced at Newark from bittern by Westvaco Chlorine Products Corporation. In order to obtain its own source of magnesia, Permanente Metals Corporation built the sea water plant at Moss Landing that is still in operation. Production began late in 1942.

In 1943, when the magnesium plants throughout the United States were approaching capacity production, it became apparent that the military demand was not as large as had been anticipated. Production was therefore gradually curtailed. The Manteca plant was closed in May 1944 and placed on a standby basis. The plant at Permanente operated through 1945 and was dismantled in 1947. Permanente Metals Corporation, now Kaiser Aluminum & Chemical Corporation, has developed markets to absorb the magnesia products produced at the Moss Landing plant, and the capacity has been substantially increased.

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## MANGANESE\*

BY FENELON F. DAVIS

Manganese-bearing rocks are widely distributed throughout California. Deposits in more than 700 localities in 44 counties have been prospected and about one-fourth of these deposits have yielded ore. Manganese ore was first mined in California in 1867 and since that date deposits in the state have yielded an estimated 263,000 short tons. Nearly nine-tenths of this production was made during World Wars I (1914-19) and II (1941-45), and during the Korean and post-Korean war period (1952-55) when prices were higher and grade requirements were lower than in peacetime.

The price of manganese ore declined following the termination of World War II in 1945, and only a token production was reported in California from 1946 through 1951. As the specifications for metallurgical-grade ore also were re-established at a minimum manganese content of 40 percent, the lower-grade ores from California deposits were no longer in demand.

A program designed to develop and produce battery-grade manganese ore was initiated at the Ladd mine in San Joaquin County during 1951. Production from this mine continued until the end of 1954.

Manganese ore from numerous deposits throughout the state also was shipped intermittently from 1952 to 1955 to the U. S. Government stockpiles at Wenden, Arizona, and Deming, New Mexico. These stockpiles were established under a program designed to encourage the production of low-grade domestic manganese ore with a manganese content in the 15 to 40 percent range. The deposits in California that contributed to this program were mostly in Imperial, Riverside, and San Bernardino Counties. High-grade domestic manganese ores (40+ percent Mn) also were purchased by the U. S. Government under a carload-lot program which ran concurrently. Such purchases are made at the railroad shipping point nearest the mine. The high-grade program has been extended to January 1, 1961.

An all-time peak production of 37,747 short tons of manganese ore valued at \$1,543,949 was reported from California in 1954. This output included ores ranging from 15 to 50 percent manganese. The quota of the two stockpiles was filled in 1955 and production declined immediately.

In 1954 shipments of manganese ore from domestic mines in the United States also reached the high point of 206,128 short tons. The extent to which this production fell short of domestic requirements is indicated by the consumption and general import figures for the same year. In 1954 domestic consumption was reported at 1,740,648 short tons and general imports at 2,166,147 short tons (DeHuff, 1956).

**Mineralogy.** Manganese is a primary but minor constituent of all igneous rocks. It is the sixteenth most common element in the earth's crust, but because of its affinity for oxygen does not occur naturally in the metallic state. The most abundant and the principal manganese ore minerals are oxides, but manganese-bearing silicates and carbonates also are common. An accurate

identification of manganese minerals in the field is difficult because many of them resemble each other, ordinarily are intimately associated, and commonly have altered from one another. The weight of the minerals (average specific gravity of oxides 4.5), and the ease with which they alter to black, sooty oxides, are the principal means of distinguishing manganese minerals from other rocks.

The principal manganese oxides are pyrolusite ( $\text{MnO}_2$ ), psilomelane ( $\text{BaMn}_9\text{O}_{18} \cdot 2\text{H}_2\text{O}?$ ), hausmannite ( $\text{Mn}_3\text{O}_4$ ), manganite ( $\text{Mn}_2\text{O}_3 \cdot \text{H}_2\text{O}$ ), and braunite ( $3\text{Mn}_2\text{O}_3 \cdot \text{MnSiO}_2$ ). Pyrolusite, with a hardness usually of 1 to 3, is a black, sooty mineral which crystallizes with a fibrous structure. Psilomelane has a hardness usually of 5 to 6, is also black, and crystallizes with a botryoidal structure. Hausmannite, which is 5 to  $5\frac{1}{2}$  in hardness, brownish-black, and shows a brown streak, occurs in compact masses that occasionally have been discarded as chert. Manganite, with a hardness of 4, is a gray to black mineral with a brown streak. It is easily identified where it occurs as prismatic crystals or needles. Braunite is 6 to  $6\frac{1}{2}$  in hardness, with brownish black color and streak. It crystallizes in small pyramids and occurs with siliceous minerals. Wad is a soft, hydrous, impure mixture of manganese oxides and clay of low specific gravity.

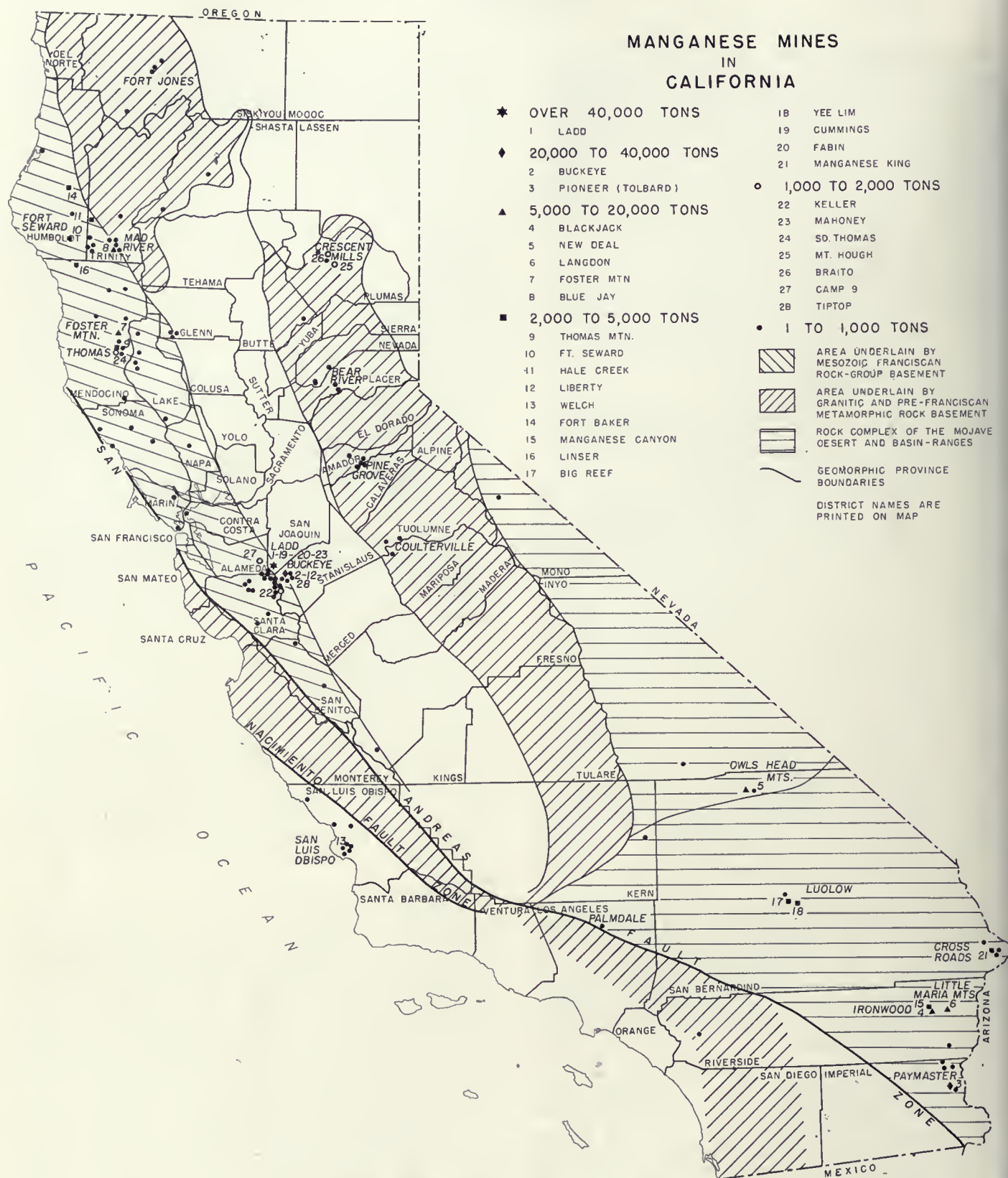
Rhodo-chrosite ( $\text{MnCO}_3$ ), a manganese carbonate, is the principal primary manganese mineral in the Coast Ranges of California. It commonly occurs as a granular mineral colored white, gray, or pale pink, with a white streak. Although its hardness is only 4.0, it is dense and tough where fine grained.

Rhodonite ( $\text{MnSiO}_3$ ), a manganese silicate, is the principal primary manganese mineral in the Sierra Nevada and in the Klamath Mountains. It has a hardness of 6, a vitreous luster and crystallizes with a bladed structure. It is similar to rhodo-chrosite in color (pink), streak, and specific gravity (3.5). Other manganese silicates include: bementite ( $5\text{MnO} \cdot 4\text{SiO}_2 \cdot 3\text{H}_2\text{O}$ ), a waxy, yellow-brown mineral with hardness of 4 to 6; neotoeite ( $\text{MnO} \cdot \text{SiO}_2 \cdot n\text{H}_2\text{O}$ ), a shiny, yellow to black manganiferous opal; spessartite ( $\text{Mn}_3\text{Al}_2 \cdot \text{Si}_3\text{O}_{12}$ ), a hard (6.5), vitreous, brown garnet which occurs in small dodecahedral crystals.

**Geologic Occurrence.** Igneous rocks and magmatic solutions are the primary source of manganese (Jenkins and others, p. 24, 1943). Although a small tonnage of manganese ore has been produced from hydrothermal vein deposits in the western United States, most of the primary manganese minerals are not sufficiently concentrated to form ore. The large ore deposits throughout the world are associated with sedimentary rocks and the ore minerals are often of secondary origin. They represent the oxidation, solution, and redeposition, or hydrothermal alteration of the original manganese-bearing minerals. Some of the hydrothermal and sedimentary deposits have been metamorphosed so that manganese silicate such as rhodonite and spessartite have formed. Manganese ore has been mined only from the oxidized parts of metamorphic deposits, because the silicates do not constitute commercial sources of manganese.

\* Extracted in part from a section prepared by Richard A. Crippen, Jr., California Div. Mines Bull. 156.







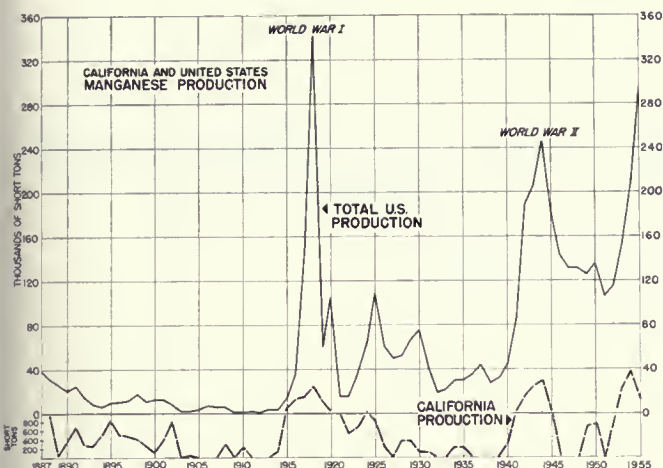


FIGURE 2. Chart showing production of manganese ore in California and in the United States.

The principal manganese deposits of India, the chief exporter of manganese to the United States during 1955, are in the Nagpier-Balaghat districts of the central provinces. According to Sully (1955) the ores consist of a mixture of psilomelane and braunite which occurs in large bodies. The Hirapur part of the Balaghat deposit is described as 40 to 50 feet thick, 400 feet wide, and  $1\frac{3}{4}$  miles long. The best grade ore averages 50 to 54 percent manganese, 6 to 8 percent iron, and 6 to 8 percent silica. Reserves in the Central Provinces have been estimated at 15 to 20 million tons of best grade ore (40 to 54 percent manganese) and several times that quantity of ore containing 30 to 40 percent manganese.

Russia, the principal exporter of manganese to the United States prior to 1942, also contains large deposits. These are mostly near Tchiaturi, Georgia, in the Caucasian Range, and near Nikopol on the Dnieper River. A pyrolusite deposit on the Mazul River in western Siberia is described by Sully (1955) as 120 feet thick in places, with a manganese content up to 47 percent and reserves of 1.6 million tons.

Most of the commercial concentrations of manganese in California are of sedimentary origin. (Jenkins and others, 1943, p. 56). Many of the deposits have been subsequently metamorphosed and have yielded very little ore. Manganese in the state also has been mined from fissure and replacement deposits of hydrothermal origin.

In California, most of the unmetamorphosed manganese deposits of sedimentary origin occur in chert of the Franciscan (Upper Jurassic?) formation which is widely exposed in the Coast Ranges. They are similar in their general features and are known collectively as deposits of the "Franciscan type." Franciscan chert is ordinarily thinly layered with shaly partings, but it locally forms large massive lenses. These lenses commonly contain valuable manganese concentrations. Some deposits are in red chert, but most of the larger bodies are in white, greenish, or buff chert. The ore bodies generally resemble elliptical pancakes in shape, and most are less than 200 feet in maximum diameter. The largest known ore body of this type in California, that at the Ladd mine in San Joaquin County, was 800 feet long.

The larger bodies generally contain cores of massive ore which grade into disseminated ore near the edges. Rhodochrosite and manganese silicate (bementite?) are the principal primary minerals (Jenkins and others, p. 57, 1943). These minerals have been altered to form "black oxide" ore through depths of as much as 200 feet.

The Franciscan ore bodies and the associated chert probably were deposited in ocean basins of restricted circulation. Although the source of the silica and manganese has been a matter of dispute, the workers whose

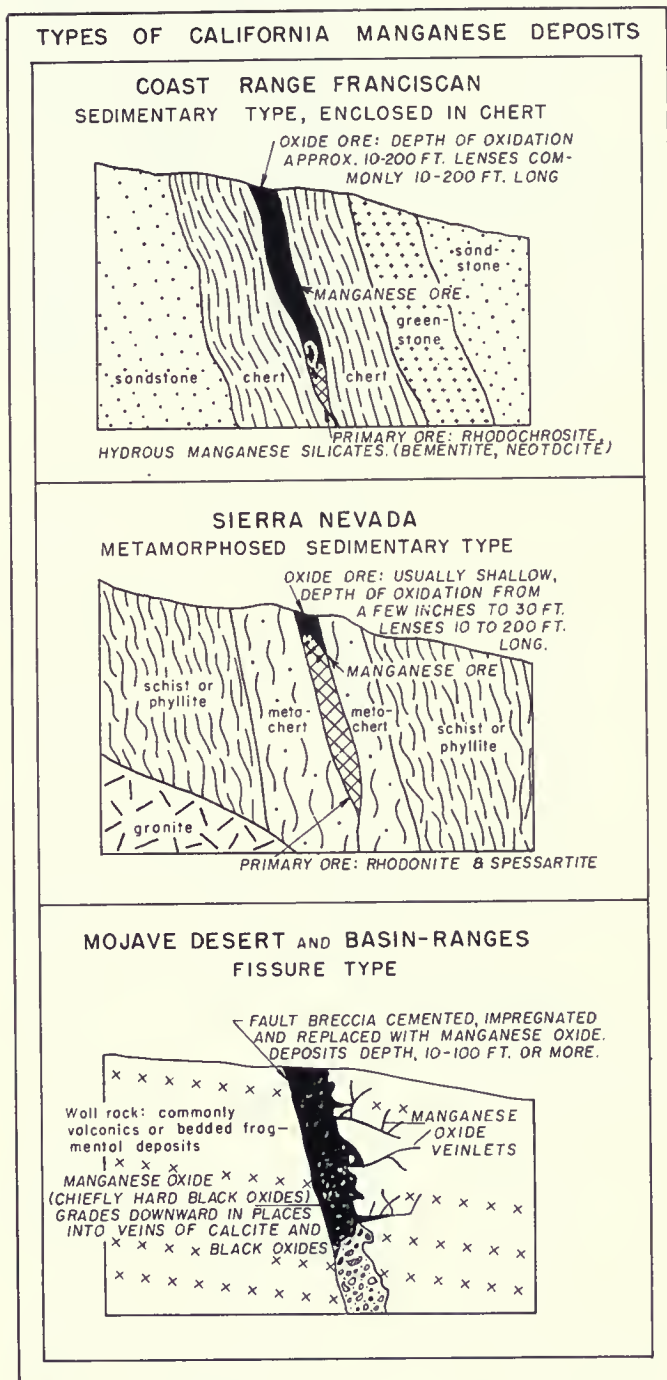


FIGURE 3. Generalized geologic cross-sections showing types of California manganese deposits. After Jenkins, 1943.



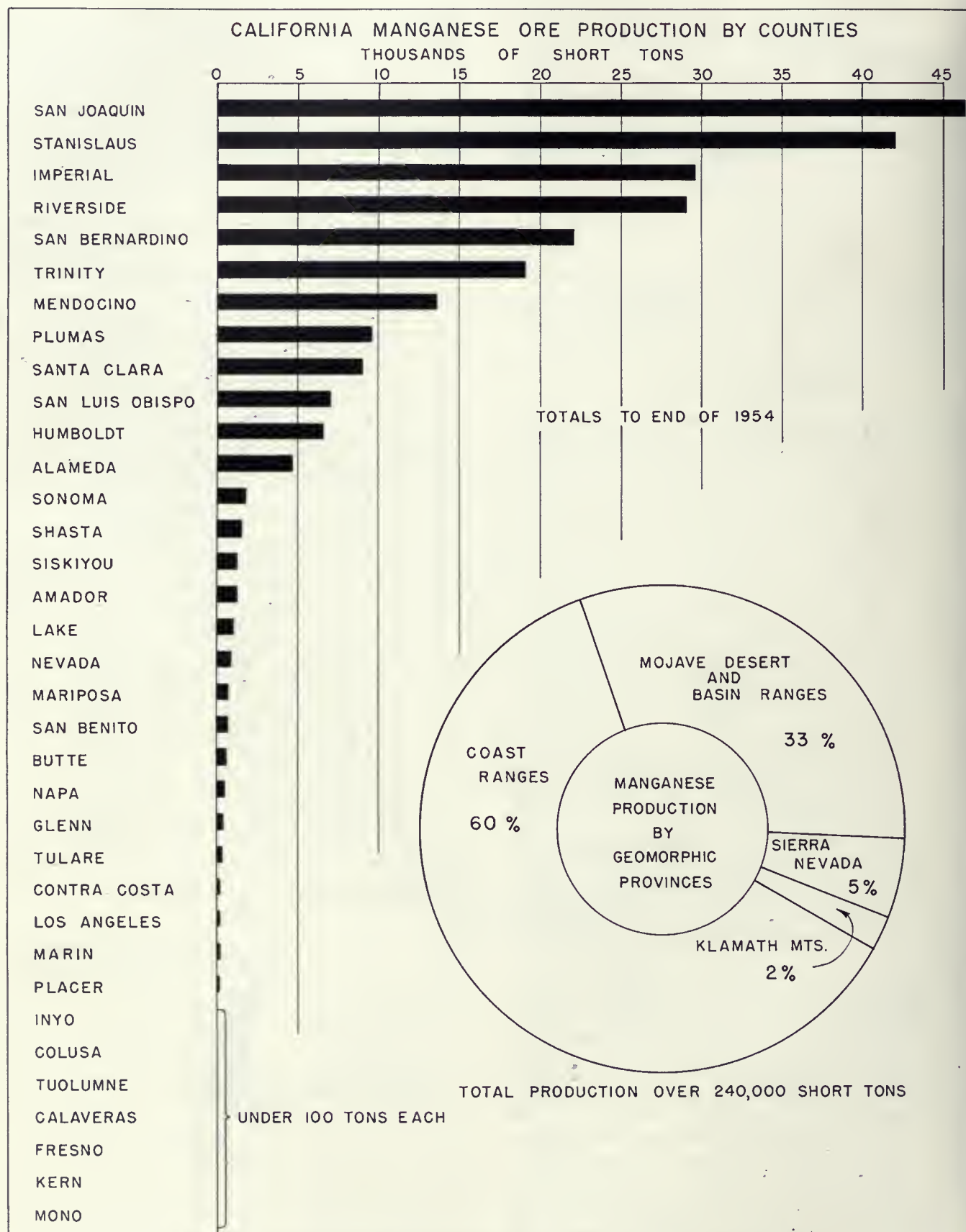


FIGURE 4. Chart showing California manganese ore production, by counties, 1887-1954.



studies have been the most comprehensive favor the concept that silica, manganese, and iron were precipitated simultaneously, and that they are of submarine volcanic origin (Taliaferro and Hudson, 1943; Taliaferro, 1943).

Metamorphosed sedimentary manganese deposits are widespread throughout the Sierra Nevada and are confined to rocks of the Calaveras (Paleozoic) and Amador (Jurassic) groups. Some deposits of this area have undergone only moderate dynamic metamorphism; others, roof pendants in granodiorites, have been intensely metamorphosed. Previous to metamorphism, these deposits appear to have been identical with the sedimentary manganese deposits of the Coast Ranges. During metamorphism the manganese carbonate has been recrystallized; siliceous manganiferous substances have formed rhodonite and spessartite. The depth of oxidation is generally very shallow and most of the deposits are currently of little economic importance.

At numerous localities in the desert regions of southeastern California, ore shoots of manganese oxides have formed in fissures that cut fanglomerate, volcanic rocks, limestone, and granite. Most of the deposits consist of brecciated zones cemented, impregnated, and partly replaced by manganese oxide.

"These shoots range from a few feet to 500 feet in length, and from a few inches to ten feet in width. The general depth of mineralization is unknown. In some places it goes as deep as 100 feet, in others less than ten feet. The ore consists principally of hard manganese oxide, similar to psilomelane, but soft oxide and a radiating mineral reported to be manganite are present. Many of the deposits contain veins of white calcite which are clearly later than the manganese. The average manganese content of the deposits mined is from 15 to 30 percent. The hard oxide can be hand-sorted in some places to give a product containing 40 to 45 percent of manganese" (Jenkins, 1943, p. 61).

In California, manganese also occurs in very low-grade bedded deposits, in replacement deposits, in manganiferous iron deposits, and in superficial deposits of several types. Most of these deposits are too small or too low grade to be of commercial importance.

*Localities in California.* Production has been recorded from about 170 of the 675 manganese localities described in California Division of Mines Bulletin 152. Sixty percent of the manganese ore production in California has been obtained from deposits in the Coast Ranges. These are grouped largely in four areas: (1) the Diablo Range south and southwest of Tracy in San Joaquin, Stanislaus, Santa Clara, and Alameda Counties; (2) the Mad River Valley area in southern Humboldt and Trinity Counties; (3) east-central Mendocino County and the adjoining part of Lake County; and (4) the western part of San Luis Obispo County. About 13 mines in these areas have each yielded more than 1,000 tons of manganese ore each.

The mines in the Ladd-Buckeye area south of Tracy have accounted for 60 percent of the manganese ore production from Coast Ranges deposits, or over one-third of the total output of the entire state. The area constitutes a northwest-trending strip 12 miles long and 2 to 4 miles wide on the western flank of Corral Hollow. It includes four mines centered around the Ladd mine



FIGURE 5. Lower adit portal and upper surface workings at the Ladd mine, San Joaquin County.

in San Joaquin County and 10 mines clustered near the Buckeye on the north slope of Mount Oso in Stanislaus County. The central part of the strip has been unproductive.

The manganese deposits occur in chert lenses in a northwest-trending belt of rocks of the Franciscan group which are more than 10,000 feet thick in this area (Trask, 1950). This group consists chiefly of massive sandstone beds separated by thin beds of shale; but also includes chert lenses, conglomerate lenses, greenstone, schist, and serpentine.

Interbedded with the shale and sandstone beds are chert lenses whose thickness varies markedly along the strike. Thick zones of chert lenses occur at both the Ladd and Buckeye mines and a much thinner chert zone is in the intervening area. The thickness of the manganese ore zones in the area vary directly with the thickness of the enclosing chert zones.

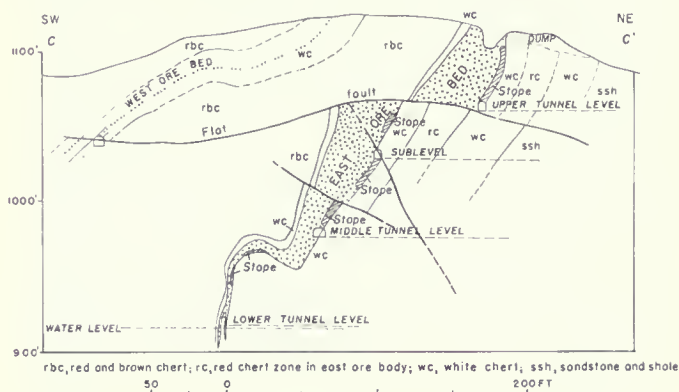


FIGURE 6. Geologic section (c-c') across the Ladd mine, San Joaquin County. After Lasky, Warren and Trask, 1941.





FIGURE 7. Middle adit portal and trestle to ore bin and dump at the Ladd mine, San Joaquin County. Photo by W. B. Clark, October, 1953.

Most of the manganese ore at the Ladd mine has been produced from the east ore body which lies in massive white chert about 50 feet above the base of the chert zone. The east ore body is 35 feet in maximum width and has been explored 800 feet along the surface and 350 feet in depth.

The primary minerals are gray rhodochrosite and bementite which have been oxidized above the ground-water level. The massive primary carbonate has contained 35 to 42 percent manganese with 10 to 15 percent silica, whereas the oxide ore contained 50 to 55 percent manganese with 10 to 20 percent silica and the disseminated ore contained 5 to 25 percent manganese with 30 to 60 percent silica (Trask, 1950). The high-grade oxide ore was mined previous to World War II. The ore mined from 1951 to 1954 ranged from 25 to 33 percent manganese oxide (Clark, 1955).



FIGURE 8. Surface cuts, adit portal, mine ore bin and truck loading facilities at the Pioneer No. 4, Imperial County.

The Ladd mine was opened in 1867 and has been worked intermittently since that time. About 10,000 tons of manganese ore were produced during World War I. The total production to 1950 was within the range of 30,000 to 50,000 (?) tons. The east ore body has been mined on four levels, numerous sublevels and in open cuts. Total length of the workings is  $4,000 \pm$  feet. The most recent work began in 1950 when the Teekay Mines Inc., a subsidiary of Taylor-Knapp Company, produced manganese dioxide for use in the battery industry. In 1951 a concentrating plant was installed to upgrade the ore by a combination of magnetic and gravity methods. Mining progressed both on the surface and underground at a total production rate of 100 tons per day. The mill delivered two battery-grade products containing 52 percent manganese dioxide and 62 percent manganese dioxide, respectively, with low iron and high silica contents. Production ceased early in 1955. The mine was closed and the mill was dismantled.

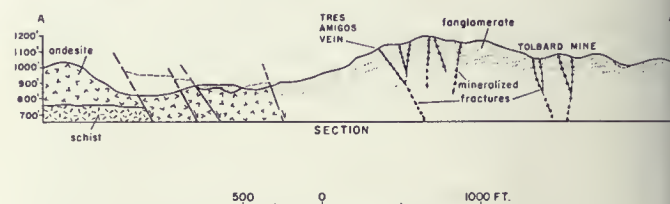


FIGURE 9. Geologic section across the Paymaster district, Imperial County. After Hadley, 1941.

The Blue Jay mine in southern Trinity County was discovered in 1941. It was one of the more productive manganese mines in California during World War II. The geological features of the manganese bodies at this property are typical of many small deposits in the Coast Ranges, although the grade of ore is considerably higher than is usually encountered.

At the Blue Jay mine, steeply dipping ore bodies 3 to 4 feet thick and 15 feet apart lie enclosed in thin-bedded white chert of the Franciscan group. The surface-exposed oxide ore grades rapidly downward into hausmannite, rhodochrosite, and bementite. The ore bodies were worked for at least 200 feet along the surface and to a depth of 50 feet. About 5,000 tons of ore averaging 50 percent manganese were shipped during World War II, and an additional small tonnage was shipped during the period 1952-55.

The principal manganese areas in the desert region of southeastern California have been the Paymaster district in eastern Imperial County; the McCoy and Little Maria Mountains districts in eastern Riverside County; and the Owls Head district in north-central San Bernardino County. The commercial manganese in these areas has been obtained from fissure deposits and the combined total production of these deposits has been about 84,000 tons. Three of the most productive mines in these districts in recent years are discussed in the following paragraphs.

The western part of the Paymaster district is covered mostly by a coarse, well-indurated, orange fanglomerate of probable Tertiary age. It overlies fractured Tertiary (?) andesite flows and a basement complex of folded schist, gneiss, and granitic dikes (Hadley, 1942).



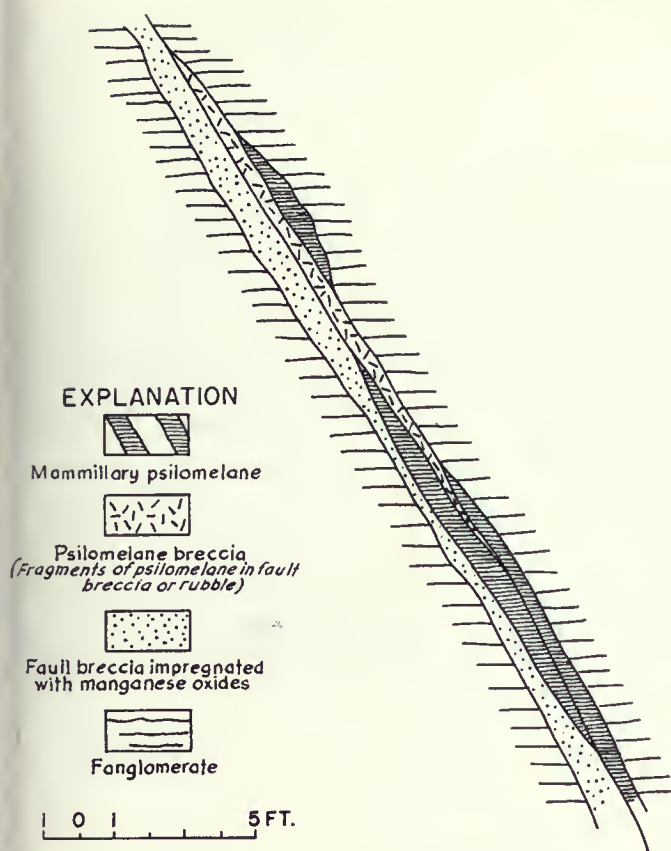


FIGURE 10. Sketch of typical vein structure, Paymaster district, Imperial County. After Hadley, 1941.



FIGURE 11. Surface cuts at the New Deal mine, Owlhead Mountains, San Bernardino County.

The volcanic rocks and the fanglomerate are traversed by numerous minor tension faults, along which veins or stringers of psilomelane, pyrolusite, and manganite have been emplaced. The width of the veins ranges from 1 inch to 3 feet. They can be traced a few hundred feet along the surface and have been mined to depths of 100 feet. Hadley (1942) estimated that the district held a relatively small tonnage of ore containing 40 percent manganese and a moderate tonnage of milling ore containing 10 to 30 percent manganese. From 1953 to 1955 ore of both grades was shipped from the Pioneer mine (Tolbard group) to the U. S. Government stockpile at Wenden, Arizona.

At the north end of the McCoy Mountains in Riverside County, volcanic flows and fragmental rocks are cut by fissures that contain lenticular ore shoots of botryoidal psilomelane. The most productive lens at the Blackjack mine is in quartz porphyry. It extends for 50 feet along the strike and for 45 feet on the dip ( $55^{\circ}$  W) with an average thickness of 4 feet. The ore has been mined through shallow underground workings and hand-sorted. Production to March 1943 consisted of 5,000 tons of ore containing 42 percent manganese and 1,000 tons of ore containing 24 percent manganese (Trask, 1950). Additional ore was mined during the period 1953-55 and was shipped to the U. S. Government stockpile at Wenden, Arizona.

In 1956 the Aspen Mining Company mined the ore and concentrated it in mills located at Inea Siding and Taseo Siding north of Blythe. The concentrate was sold to General Services Administration under the earlot program.

At the Langdon deposit in the Little Maria Mountains north of Blythe, botryoidal psilomelane occurs as segregations and veinlets along fissures and brecciated zones in limestone which is interbedded with quartzite and quartz-mica schist. A wide ore zone composed of individual veinlets as much as 3 inches thick extends for half a mile along the strike. Development consists of open cuts and shallow underground workings. Careful sorting has produced a few thousand tons of ore containing 40 percent manganese (Trask, 1950). During the period 1953-55 a small tonnage of low-grade ore from the Langdon deposit was concentrated in a gravity mill at Inea



FIGURE 12. East workings at the Big Reef mine, San Bernardino County. Loading ore from a manganese lens capped by volcanic rock.





FIGURE 13. Mill at Poe's Siding erected to treat ore from the Big Reef mine. Mine ore at left was conveyed to mill bin in center and treated entirely by jigs in center building. Mill tailings at right.

Siding, 20 miles north of Blythe, and shipped to the U. S. Government stockpile at Wenden, Arizona.

**Mining.** The manganese mines in California generally have been developed by standard methods. Manganese outcrops are opened by shallow pits or trenches along the surface exposure. The extent and attitude of the soil-covered parts of the mineralized zone is determined by cross-trenches or bulldozer cuts. The wider deposits are mined in open pits; whereas narrow, steeply dipping ore bodies require underground methods.

If the topography permits, a drift may be run along the ore body at a level lower than the outcrops, or a short cross-cut adit may be run to the ore; otherwise a shaft is ordinarily sunk in the widest and richest part of the outcrops. The development levels are connected by raises in ore along the footwall and the ore body is stoped-out

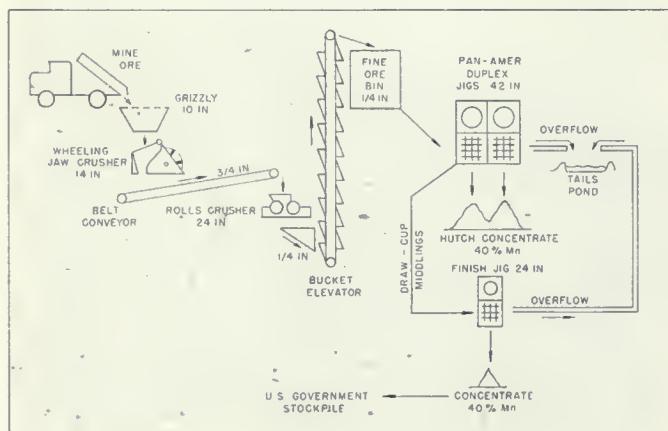


FIGURE 14. Flowsheet of manganese ore mill treating free-breaking oxides from desert breccia deposits, Ripley, Riverside County.

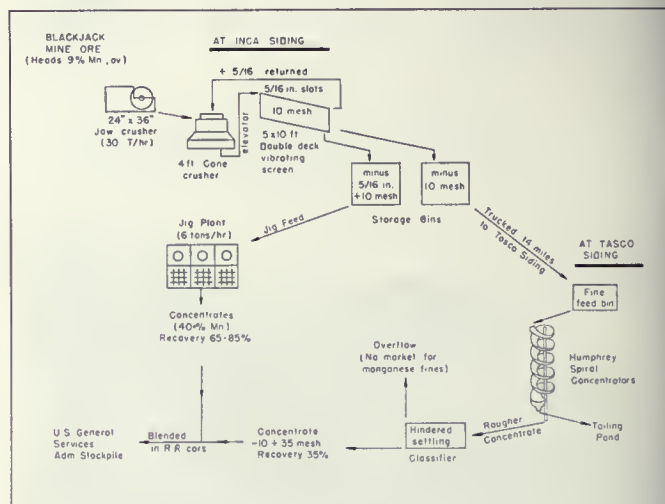


FIGURE 15. Flowsheet of manganese concentrator at Inca Siding, Riverside County, treating Blackjack mine ore.

between levels. The smaller deposits are mined by open stopes and the walls are supported by stulls or pillars. Shrinkage or sub-level mining methods commonly are employed in the larger deposits.

**Milling.** Hand-sorting is the only treatment applied to much of the manganese ore mined in California, although the ore from many of the deposits requires further beneficiation. The black oxides, pyrolusite and psilomelane, in simple association with one or more gangue minerals (chert, quartz, chalcedony, opal, limonite, calcite, and clay) can be concentrated by most beneficiation methods (fig. 14). Such ores are amenable to gravity separation, jigging, magnetic separation, flotation and the sink-float process. Concentrating tables are commonly





FIGURE 16. Mill near Ripley, Riverside County.

used because they are comparatively simple to operate. Jigging followed by flotation, spiral concentration or sink-float methods can be applied to coarse sized ore.

Some of these principles were successfully applied to California ores during the period of federal government stockpiling, 1951-56. The mills were located near Newberry, San Bernardino County; near Ripley and Blythe, Riverside County.

In many of the manganese deposits of California, however, siliceous minerals are intimately interlocked with the manganese oxide minerals, thus making separation difficult if not impossible. The liberation of the manganese minerals from such a mixture requires a fine grinding which promotes the formation of undesirable slimes. Sliming produces a small concentrate fraction and a large middling fraction, consequently a costly re-grind circuit is required. The successful small-scale flotation of such siliceous ores also has been retarded by the absence of collectors of sufficient selectivity.

Although little rhodochrosite ore has been produced in California, it is amenable to a flotation process that employs fatty acid collectors. Rhodochrosite is crystalline, easily cleavable, and not subject to sliming. Fine grinding can therefore be employed to obtain maximum liberation of the mineral. Sink-float treatment or jigging commonly precedes fine grinding to reject as much gangue as possible at a coarse size. Subsequent sintering of the flotation concentrate is essential and increases the grade of the concentrate by removing the  $\text{CO}_2$  as a gas (Schack and Poole, p. 6, 1947).

Magnetic separators can be successfully used on iron-bearing manganese ore. A preliminary reduction roast may be necessary to render the iron minerals susceptible to attraction by a low-intensity magnetic field. Fine grinding also may be required as the manganese and iron commonly are intimately associated. Magnetic recovery on the fine sizes may involve increased expense for additional magnetic units, owing to the comparatively low handling capacity of each separator for fine feed (Schack and Poole, p. 16, 1947).



FIGURE 17. Adit portal and steep-dipping vein at the Blackjack mine, Riverside County. Country rock is brecciated quartz porphyry.







Table 1. *Uses of manganese.\**

		USE OR PRODUCT	FORM USED	
METALLURGICAL	FERROUS	Alloy in high-grade steel Purifier in smelting	{ Ferromanganese Spiegeleisen High manganese pig iron	96%
	NON-FERROUS	Alloys with copper, aluminum, nickel, zinc, tin, lead, magnesium, iron, etc. Purifier in smelting nearly all known alloys	Ferromanganese	
CHEMICAL	DRY CELL	Depolarizer in dry cells	Manganese dioxide	4%
	PAIN'T AND VARNISH	Green and violet color Drier	{ Barium manganate Manganese metaphosphate	
	INKS	Drier	{ Manganese borate, linoleate, naphthenate, oleate, resinates and talleate.	
	CERAMICS	Coloring material	Manganese sulfate and nitrate Manganese chloride Lithium manganate	
	CHEMICAL	Oxidizer in manufacture of organic products Oxidizer in manufacture of hydroquinone, chlorine, bromine, and iodine Purifying gases Laboratory chemicals	Manganese persulphate Manganese dioxide Potassium permanganate Potassium permanganate and various other compounds	
	TEXTILE	Brown or bronze dye Bleach	Manganese chloride Potassium permanganate	
	MISCELLANEOUS	Disinfectant Fertilizer-agricultural minerals Insecticide Welding rod coating Protective coating on steel Porcelain enamel Jewelry and ornamental stones	Potassium permanganate Manganese sulphate Manganese arsenate { Manganese carbonate Manganese dioxide Manganese phosphate Manganese dioxide Rhodonite	

\* Revised from Jenkins, 1943.



creases the strength and hardness of steel and imparts properties that allow it to be rolled and forged more easily.

In 1955 the domestic consumption of manganese ore in the United States totaled 2,378,000 short tons (De Huff, 1956). About 96 percent of this ore was consumed in the metals industry. Since manganese steel is hard, tenacious, and ductile, it is valuable for many purposes that involve constant wear. It is used for dipper teeth on steam shovels, dredger pins, crushing and grinding machinery, elevator links, agricultural implements, railroad rails, wheels and axles, burglar-proof safes, and for many other items.

Most of the ore thus used is first smelted in a blast furnace or an electric furnace and converted into ferromanganese, an alloy containing 78 to 82 percent manganese, 8 to 15 percent iron, 0.5 to 1 percent silicon, 5 to 7 percent carbon, and minor quantities of phosphorus and sulfur. The lower-grade manganese alloys—spiegel-eisen (18 to 22 percent manganese, 70 to 80 percent iron, and 5 to 6 percent carbon) and silico-manganese (65 to 70 percent manganese, 12 to 25 percent silicon, the remainder iron and carbon)—are also commonly used but less extensively so than ferromanganese. These three alloys, especially ferromanganese, are essential to the steel industry. About 14 pounds of manganese are used in each ton of steel.

Manganese metal, refined to 99.9 percent purity, has recently become a competitor of ferromanganese. It is produced chiefly by the electrolysis of acid solutions of manganese ore. The manganese dioxide is first reduced to the soluble monoxide which is treated with sulfuric acid. The high purity of electrolytic manganese makes it especially desirable as an alloying element in making stainless steel, alloy steels, and non-ferrous alloys.

During the 1930's, a commercially feasible electrolytic process was developed by the United States Bureau of Mines and put in pilot-plant operation at Boulder City, Nevada. This plant utilized low-grade ore, averaging 20 percent manganese, from deposits in several western states, including ore from the Ladd mine in San Joaquin County, California. Nearly 1½ million pounds (750 tons) of electrolytic manganese had been produced by May 1946, when the project was completed and the pilot plant ceased operation.

In 1939 a commercial plant, based on the design of the United States Bureau of Mines pilot plant, was set up at Knoxville, Tennessee, by a private firm, the Electro-Manganese Corporation. This plant included improvements that permitted large-scale production. The planned capacity was 450,000 pounds per month, and actual production reached 4½ million pounds (2,250 tons) for the year 1948. By 1956, the capacity of the plant had reached 7,000 short tons per year. Manganese metal also can be produced by smelting high-grade ore in an electric furnace.

About 2½ percent of the manganese ore consumed in the United States is used in the manufacture of dry-cell batteries. The ore for this purpose must be high in available oxygen. Only the manganese dioxide minerals meet this requirement, since the available oxygen in them is so loosely combined that it can be liberated by heat or chemical action.

The dry cell consists of a zinc container (negative pole) filled with manganese dioxide through which an electrolyte of ammonium chloride is diffused. When current is drawn from the cell, the ammonium chloride dissociates into ammonia, chlorine, and hydrogen gases. The chlorine combines with the zinc to form a zinc chloride salt. The ammonia combines with the zinc chloride to form zinc ammonium chloride salt. The hydrogen collects at the carbon electrode (positive pole) in the center of the cell where it forms a non-conductive film and stops the flow of current. The manganese dioxide is a depolarizer which breaks or prevents formation of the film and permits the current to flow continuously. In this action the oxygen combines with the hydrogen to form water and the end product is probably  $Mn_2O_3 \cdot H_2O$ .

The manganese ore to be used in battery manufacture also should be low in metals such as iron, lead, copper, nickel, cobalt, and arsenic, which react electrolytically with zinc and corrode the container. Ores from many of the Franciscan-type deposits of the Coast Ranges have proved suitable for this use.

During and following the Korean War period 1950-56, considerable progress was made in the electrochemical production of "synthetic manganese dioxide" from moderate to low-grade crude ores. In this process manganese ore (40+ percent  $MnO_2$ ) is reduced to manganese monoxide to convert the manganese to soluble form. The manganese monoxide is then treated with sulfuric acid to yield liquid manganese sulfate which is piped to electrolytic cells. In the cells manganese dioxide is deposited on the graphite anodes. The shells, which contain 95 percent  $MnO_2$  are crushed and ground to 95 percent minus 200 mesh. This product is consumed in the manufacture of batteries for military use under especially strenuous conditions and is currently considered too costly for metallurgical use. In 1955, production ranged from 10 to 15 tons per day.

Other phases of the chemical industry account for about 1½ percent of the total U. S. consumption of manganese ore. Here, too, the manganese ore acts as an oxidizer in that it yields part of its contained oxygen under heat or acid treatment. It is used in the manufacture of such products as ink, paint, and varnish driers, textile coloring agents and bleaches, agricultural chemicals, ceramic coloring agents, and laboratory chemicals.

Manganese dioxide is converted into manganese sulfate which is the base for many important driers in the paint industry. Manganese driers function as oxidation catalysts and produce films that are hard, brittle, and resinous. They are widely used in floor varnishes where hardness is essential.

Small quantities of manganese dioxide are used in the ceramic industry to produce black, brown, and purple colors in glazes, enamels, and brick. Welding-rod coatings commonly include manganese dioxide or manganese carbonate which produce a brittle, fluid slag, and replace manganese volatilized in the welding arc.

Since manganese has several chemical valences (2, 3, 4, 6 and 7), it forms a wide variety of chemical salts such as the green pigment barium manganate, and the manganese arsenite which is an insecticide.



The beautiful pink shades of the mineral rhodonite in combination with the black oxides make it highly desirable for jewelry and as architectural ornamental stone.

*Consumption of Manganese Ore in California.* During the period 1951-56, the General Services Administration of the U. S. Government has dominated the manganese purchase picture in California. The low-grade ores (minus 40 percent Mn) have been shipped to General Service Administration stockpiles at Wenden, Arizona, and Deming, New Mexico, and probably will eventually be concentrated and upgraded to metallurgical grade. The high-grade metallurgical ores (plus 40 percent Mn) have been purchased in carload lots at the railhead nearest the mine and shipped to permanent Army strategic stockpiles at Avondale, Colorado, and Fort Worth, Texas. None of this ore has gone into industry.

During this period the California steel industry has substituted ferromanganese for ore almost entirely. Steel making is thus facilitated and the end products are more easily controlled, as ferromanganese is of uniform composition whereas manganese ore generally is variable. Ferromanganese for California steel is made mostly in plants in the eastern United States, Portland, Oregon, and Butte, Montana. Ferromanganese also is imported from India and Japan. Steelmakers in California formerly used manganese ores imported from Mexico, Philippine Islands, India, and South Africa, and supplemented them with ore from California.

Keen competition from foreign battery-grade ores and synthetic manganese dioxide, together with the high cost of underground mining and high freight rates to eastern and mid-western battery manufacturing plants, eventually forced closing of the California mines that were supplying battery grade ore to commercial outlets. No battery manufacturing plant is presently located west of Sioux City, Iowa (1956).

None of the chemical plants in California uses manganese ore. Prime manganese chemicals such as manganese acetate, manganese chloride, and manganese sulfate are manufactured elsewhere. Manganese sulfate (98 percent) is imported into California and used in the chemical process industries. Among the paint, varnish, and ink driers manufactured in California are manganese borate, manganese linoleate, manganese naphthuate, manganese oleate, manganese resinate, and manganese talleate.

Manganese sulfate is used also as an agricultural mineral in California where a manganese deficiency has been noted in apricot, peach, walnut, and citrus trees. This deficiency has often been corrected by sprays or by the direct injection into the tree trunks themselves. The annual tonnage of manganese sulfate used for this purpose has been very erratic in recent years. Variations from 592 tons in 1950 to 41 tons in 1954 have been reported by the Bureau of Chemistry.

*Marketing.* Metallurgical manganese is purchased on the basis of a long ton (2,240 pounds) of dry ore. As all ore contains some moisture, commonly as much as 15 percent, a moisture deduction must be made from the total weight of each shipment. Prices on metallurgical ore containing over 35 percent manganese are quoted on the basis of units of contained manganese.

The chemical industry purchases ore on a short ton (2,000 pounds) basis with a minimum requirement of manganese dioxide. An analysis may therefore report the ore in percentage of manganese dioxide. As pure manganese dioxide contains 63.2 percent manganese, it will be necessary to multiply the manganese dioxide content of the ore by 0.632 if the manganese content (or number of units of contained manganese) is desired.

"Ferruginous-manganese" is a term often applied to iron-bearing ore containing 10 to 35 percent manganese. Such ore is usually purchased on the basis of the total content of iron and manganese, and the current price per ton for equivalent grade iron ore.

Iron ore containing less than 10 percent metallic manganese may be termed manganiferous iron ore. The term manganiferous ore is often applied to any material with a manganese content in the 10-to-35 percent range.

*Specifications for Ferro-Grade Ore.* The steel industry has established certain specifications for metallurgical or ferro-grade manganese ore:

Average metallic manganese content.....	48 percent by weight
Iron .....	6 percent
Silica and alumina (insoluble), max.....	11 percent
Phosphorus, max. ....	0.12 percent

Zinc, tin, lead, and copper are undesirable and no sodium or potassium should be present. Ores with a manganese content as low as 40 percent can be mixed with higher-grade ores, providing the manganese-iron ratio does not exceed  $7\frac{1}{2}$  to 1. Lump ore ranging from 5 inches down to a plus 20 mesh size is most desirable. Fines should not exceed 5 percent minus 20 mesh.

Possible buyers of metallurgical grade manganese ore include:

Bethlehem Pacific Coast Steel Co.  
20th and Illinois Sts., San Francisco  
Bradley & Ekstrom  
320 Market St., San Francisco  
Ohio Ferro-Alloys Corp.  
Canton, Ohio  
Columbia-Geneva Steel Division  
U. S. Steel Corporation  
141 Battery St., San Francisco

The following quotation on manganese ore is taken from the Engineering and Mining Journal, Metal and Mineral Market report of March 7, 1957:

Indian ore, \$1.64 @ \$1.69 per long ton unit of Mn, c.i.f. U. S. ports, import duty extra, basis 46 to 48% Mn, nearby positions.

On long-term contracts for ore from various sources 46%-48% Mn, quotations are nominal.

*Specifications for Chemical or Battery-Grade Ore.* A chemical analysis is not entirely satisfactory in determining the suitability of manganese for making batteries. Oxide ores are required, but ores of similar chemical composition do not give the same results in actual usage. The selection of battery-grade ore is best made by means of a set of test cells of various ore samples. The operating characteristics of each sample set is then determined over a period ranging from 3 to 24 months. Research now under way, utilizing x-ray photographs of the ore, may eliminate the time-lag. Meanwhile, the following tentative specifications have been established.



Available oxygen or MnO <sub>2</sub> —	75 percent min.
Total manganese, Mn ———	48 percent min.
Iron, Fe —————	3 percent max.
Silica, SiO <sub>2</sub> —————	5 percent max. (chemical grade)
Silica, SiO <sub>2</sub> —————	25 percent (battery grade)
Absorbed moisture, H <sub>2</sub> O ———	5 percent max.
Cu, Cd, Ni, Pb, Sn, etc. (total) —————	0.2 max.

The ore also should be hard and porous.

Possible buyers of battery grade ore are:

General Dry Batteries, Inc.	Cleveland, Ohio
Union Carbide and Carbon Co.	30 East 42nd St., New York, N.Y.
Ray-O-Vac Co.	Madison, Wisconsin
Bright Star Battery Co.	Clifton, New Jersey
Aeme Battery Co.	59 Pearl St., Brooklyn, N. Y.
Burgess Battery Co.	Freeport, Illinois
E. J. Lavino & Co.	1528 Walnut St., Philadelphia, Pa.

The Engineering and Mining Journal, Metal and Mineral Market Report of January 3, 1957, quotes:

Manganese dioxide, 84% MnO<sub>2</sub>, long tons, bulk, c. i. f. U. S. ports, \$92 @ \$100.

*U. S. Government Stockpile Depots Purchasing Program.* On July 21, 1951, the General Services Administration announced a government purchase program of manganese ore at depots in Butte and Philipsburg, Montana, and in Deming, New Mexico. On May 5, 1953, another depot was established at Wenden, Arizona. Ore purchased under this program was required to contain a minimum of 15 percent manganese, except at Butte, where 12 percent minimum grade was established.

Ore was purchased on delivery according to the following schedule. At Deming, \$6.10 per long ton for 15 percent ore. At Butte, \$6.05 per long dry ton for 12 percent ore with payments ranging up to \$40.42 for 30 percent ore. At Philipsburg \$6.43 per long dry ton for 15 percent ore with payment ranging up to \$34.81 for 30 percent ore.

The following prices were paid for manganese ore delivered f. o. b. depot, Wenden, Arizona:

% Mn in ore	Price of 1 long dry ton
15 —————	\$8.54
20 —————	17.20
25 —————	26.94
30 —————	40.60
35 —————	56.29
40 fines —————	78.00
40 ore —————	88.00

The program originally designed to terminate on June 30, 1956, was extended to June 30, 1958, or until 18,000,000 long-ton units of manganese have been purchased, whichever occurs first.

The quota of 6,000,000+ long-ton units for the Wenden stockpile was filled and the stockpile was closed in April 1955. A similar quota for the Deming stockpile was reached and the stockpile closed in November 1955. Only the depots at Butte and Philipsburg, which had reached about half their combined quota of 6,000,000+ long-ton units, remained open in March 1957.

For further information address the General Services Administration, 49 Fourth Street, San Francisco 3, California.

*U. S. Government Carlot Rail-Head Program for Small Domestic Producers.* The General Services Administration on July 7, 1952, announced a new program of purchasing metallurgical-grade manganese ore from domestic sources. A base price of \$2.30 a long-ton unit, f. o. b. railroad car, in carload lots, is paid for ore running 48 percent manganese (Mn) with maximum 6 percent iron (Fe); 11 percent silica plus alumina (SiO<sub>2</sub> + Al<sub>2</sub>O<sub>3</sub>); and 0.12 percent phosphorus (P). Premiums are paid for better grades and penalties are levied for lower grades. Minimum grade acceptable is 40.0 percent manganese (Mn) and a maximum 16.0 percent iron (Fe); 15.0 percent silica plus alumina (SiO<sub>2</sub> + Al<sub>2</sub>O<sub>3</sub>); 0.30 percent phosphorus (P); and 1.0 percent copper plus lead plus zinc (Cu + Pb + Zn), maximum 0.25 percent copper.

The quota on this carlot program was originally set at 19,000,000 long-ton units. In 1956 the quota was expanded to 28,000,000 long-ton units and the termination date was extended to January 1, 1961. Any person in California who wishes to sell manganese ore under this carlot plan should contact General Services Administration, Regional Office, 49 Fourth Street, San Francisco, California.

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## MERCURY\*

By FENELON F. DAVIS

Approximately 88 percent of the mercury produced in the United States has been obtained from deposits in California which lie mainly in the Coast Ranges. From the beginning of recorded production in 1850 to the end of 1955, the mercury mines of California produced more than 2½ million flasks valued at over \$159,000,000. Only gold and copper, among the metallic mineral commodities of the state, have exceeded mercury in value of production.

During World War II slightly more than 70 percent of the domestic mercury production came from California sources, which in the period 1942-45 contributed 113,195 flasks valued at \$17,607,320. The 33,948 flasks produced in 1943 represented the highest annual output since 1895. From 1944 to 1950, mercury production dropped sharply, a decline caused largely by the difficulty encountered by domestic operators in meeting foreign competition following World War II. The output of mercury from California mines in 1950 was the smallest in 28 years. Meanwhile the United States was accumulating stocks of this strategic metal from foreign sources.

A renewed stimulus to mercury production was provided in 1950 by the Korean War demand and in 1951 by a U. S. Government program to encourage mercury mine exploration. By 1954 the U. S. Government and many foreign governments had embarked upon atomic energy programs which are rumored to be responsible for a reduction in the available supply of mercury. In addition, the U. S. Government in 1954 instituted a 3½-year fixed-price mercury purchase program which tended to stabilize the market and encourage the development of the mines.

Most of the early production of mercury in California was used in the amalgamation of gold, but in recent years it has found greater use in the manufacture of chemicals, in industrial instruments, in electrical apparatus and in agriculture.

*Mineralogy and Geologic Occurrence.* Cinnabar (HgS) is by far the most important ore mineral of mercury, but native mercury and metacinnabar (HgS) occur in economic quantities. More than 20 other minerals also contain mercury. Of these, amalgam (AuHg), tiemannite (HgSe), coloradoite (HgTe), calomel (HgCl), egglestonite (Hg<sub>4</sub>Cl<sub>2</sub>O), and montroydite (HgO), have been noted in California.

Cinnabar is recognized by its red color, red streak, high specific gravity, and adamantine luster. Metacinnabar, a black mercuric sulfide with a black streak, is less common than cinnabar. Native mercury, a silver-colored liquid, has been found in vugs in many California deposits.

Throughout the world, mercury deposits are confined largely to regions of Tertiary or Quaternary volcanic activity. As the mercury mineralization is of relatively low temperature, and few commercial bodies exceed 2,000 feet in depth, the deposits are classed as epithermal.

Mercury ore bodies are irregular and contain cinnabar or metacinnabar that fill fractures or voids, or have replaced the host rock. Schnette (1937) shows that many ore bodies have been formed by the concentration of primary minerals in porous rocks capped by relatively impervious rocks. Others are replacement deposits of silica-carbonate and related rocks; still others have been deposited at or very near the surface by hot springs. Bodies of disseminated ore exist at some mines.

Mercury deposits contain few other metallic minerals. Pyrite or marcasite is generally present, and stibnite is locally abundant. The principal gangue minerals are quartz, opal, chalcedony, calcite and dolomite.

Slightly over 50 percent of the larger mercury deposits in California occur in altered serpentine (silica-carbonate rock), and an additional 30 percent occur in the sedimentary rocks of the Franciscan group (Upper Jurassic?) with which the serpentine is associated.<sup>1</sup> Mercury ores also occur in the Knoxville (Upper Jurassic) sedimentary rocks, and in younger Lower Cretaceous sedimentary and Tertiary volcanic rocks. Relatively small amounts of cinnabar have been obtained from hot springs and placer deposits in the state.

The high degree of fracturing in the Franciscan rocks and in the serpentine has favored deposition in these rocks. In general the mercury minerals have formed in the interstices of porous or brecciated rocks. In many places the ore is especially rich beneath such impervious material as fault-gouge, clay shale, or dense volcanic rock. The silica-carbonate rock with which many deposits of mercury minerals are associated is commonly called "quicksilver rock." This rock is an alteration product of serpentine and is composed largely of chalcedony, quartz, and various carbonates. It is more widespread than the mercury mineralization, however, and cannot be used as a reliable prospecting guide.

*Localities.* Twenty-nine of the 30 mines that have been the most consistent sources of mercury in California are in the Coast Ranges, and are, in general, confined to areas underlain by rocks of the Franciscan group and associated serpentine. Within this province are 23 mercury districts which are scattered along a 350-mile belt extending from central Lake County southeastward to southeastern Santa Barbara County. Three of these districts, the New Almaden in Santa Clara County, the Mayacmas in Sonoma and Lake Counties, and the New Idria in San Benito County, have been the principal sources of mercury in North America. The Knoxville district in Lake and Napa Counties, the Clear Lake and Guerneville districts in Lake County, and the Oceanic district in San Luis Obispo County, also have been very productive.

Other districts in the Coast Ranges that contain mercury mines with sizeable outputs are: Wilbur Springs, and Vallejo in the counties north of San Francisco Bay; the Mount Diablo in Contra Costa County; and the Adelaida in San Luis Obispo County.

Coast Ranges mercury districts with moderate outputs are: the Oakville in Napa County; the Stayton in Mer-

\*Extracted in part from a report by Richard A. Crippen Jr. in California Div. Mines Bull. 156.

<sup>1</sup>Edgar H. Bailey, personal communication.



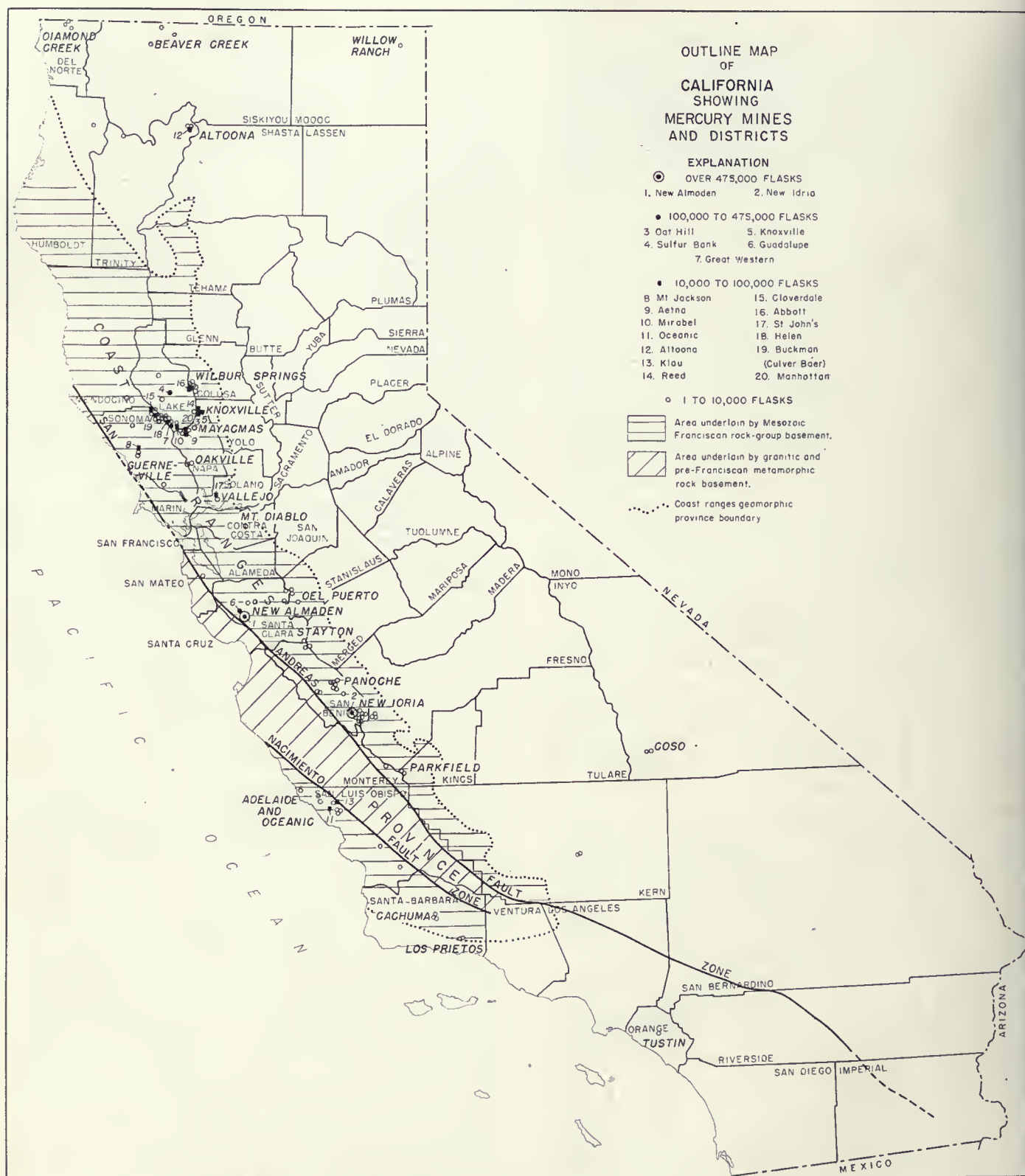


FIGURE 1. Map of California showing the location of mercury mines and the principal mercury districts.



eed, San Benito, and Santa Clara Counties; the Panoche in Fresno and San Benito Counties; the Parkfield in Kings and Monterey Counties; the Pine Mountain and the Rinconada in San Luis Obispo County; and the Caehuma and Los Prietos in Santa Barbara County. Small quantities of mercury have been obtained also from the following districts in the Coast Ranges: the Del Puerto district in Stanislaus County, the San Carpojarro district in San Luis Obispo County, the Redwood City district in San Mateo County and the Petaluma district in Marin County.

One of the state's principal mercury mines, the Altoona in northeastern Trinity County, is in the Klamath Mountains province. Another mine, the Walibu, is in the southern end of the Sierra Nevada province. Relatively small amounts of mercury also have been obtained from the following districts outside the Coast Ranges province: the Diamond Creek district of northern Del Norte County; the Beaver Creek district of northern Siskiyou County; the Coso district of southwestern Inyo County; and the Tustin district of Orange County.

The New Almaden mine a few miles south of San Jose in Santa Clara County yielded 1,051,041 flasks of mercury valued at \$49,436,161 to the end of 1951. This is more than one-third of the entire United States' production, and makes New Almaden the most productive mercury mine in North America. The peak of production was reached in 1865. Since 1946 production has been small and irregular. The New Almaden mine area, studied in detail by E. H. Bailey (1951), is underlain mostly by rocks of the Franciscan group of Jurassic (?) age. These include graywacke, arkose, sandstone, shale, conglomerate, limestone, chert, greenstone (altered lavas, tuffs and breccias) and some metamorphic rocks.

The area contains a northwest-trending anticline whose southwest limb has been highly sheared. Two major sills of serpentine appear to have been intruded up the north limb, to have converged near the crest, and to have continued down the southern flank. At the point of convergence the intrusives apparently "broke through" to higher points from which thin tongues of serpentine extended downward along the flanks of the fold. Subsequently much of the serpentine was hydrothermally altered to silica-carbonate rock, which is most abundant along the margins of the sills and tongues. Finally cinnabar, the principal ore mineral, was introduced in alkaline solution and replaced the silica-carbonate rock along a series of northeast trending fractures to form the large, rich ore bodies.

The near-surface ore bodies were formed along the thin tongues of altered serpentine. The deeper ore bodies were formed along the margins of the two altered serpentine sills. The largest ore body mined was 200 feet wide, 15 feet thick, and 1500 feet on the dip. Cobbed ore mined during the first 15 years of recorded production averaged more than 20 percent mercury. The ore produced during the entire productive history of the mine averaged slightly less than 4 percent mercury (Bailey, 1951). The workings at the New Almaden mine reach a point of 2450 feet below the surface, but almost half of the ore was removed above the 800-level.

The New Idria mine, in the southeastern corner of San Benito County, ranks second in production among mercury operations of North America. During the



FIGURE 2. View northeastward toward headframe, ore treatment plant, and dumps at the Abbott mine, Wilbur Springs district, Lake County. Underground exploration has been highly successful at this mine in recent years.

period 1858 to 1955 the mine produced nearly half a million flasks with a total value of about 35 million dollars.

The rocks exposed in the New Idria district consist of a central core of serpentine and Franciscan sandstone (Upper Jurassic?) surrounded by Panoche shale and sandstone (Upper Cretaceous) and Tertiary sedimentary rocks. Structurally the rocks form a northwest-trending, eroded, asymmetric, anticlinal dome in which the serpentine core is believed to have been pushed upward as a plastic plug (Eckel and Myers, 1946). The serpentine-Franciscan contacts and the Franciscan-Panoche contacts are marked by steep faults which dip away from the central core, except near the New Idria mine. Here, on the northeast flank of the dome the upper Panoche shales are crumpled and overturned beneath the New Idria thrust fault which has caused them to be overridden by Franciscan sandstone and serpentine.

Irregularities in the plane of the thrust fault control the shape of the underlying zone of altered and indurated Panoche rocks and the shapes of ore bodies which they contain. Veins and stockworks of fractures filled with cinnabar constitute most of the ore. Rich ore bodies have formed where the fracturing has been most intensive.

Ore has been produced at the New Idria mine through a vertical range of more than 1400 feet and through a horizontal distance of about 2000 feet. According to Eckel and Myers a large near-surface ore body extended for 800 feet in length, 150 to 300 feet in depth and was 50 to 200 feet thick. They believe it was controlled chiefly by the flattening of the New Idria thrust fault near the surface. The richest ore body was 800 feet in depth, 300 feet long and 25 to 150 feet thick. This ore-shoot occupied a steep inverted trough at the intersection of the New Idria thrust fault with a tear fault. During the period 1953-1956 exploration loans from the Defense Minerals Exploration Administration of the U. S. Government have been instrumental in uncovering new cinnabar ore bodies in the westerly extension of the mine workings.

The other mines of the Coast Ranges are too numerous to be listed individually here, but an extensive pre-



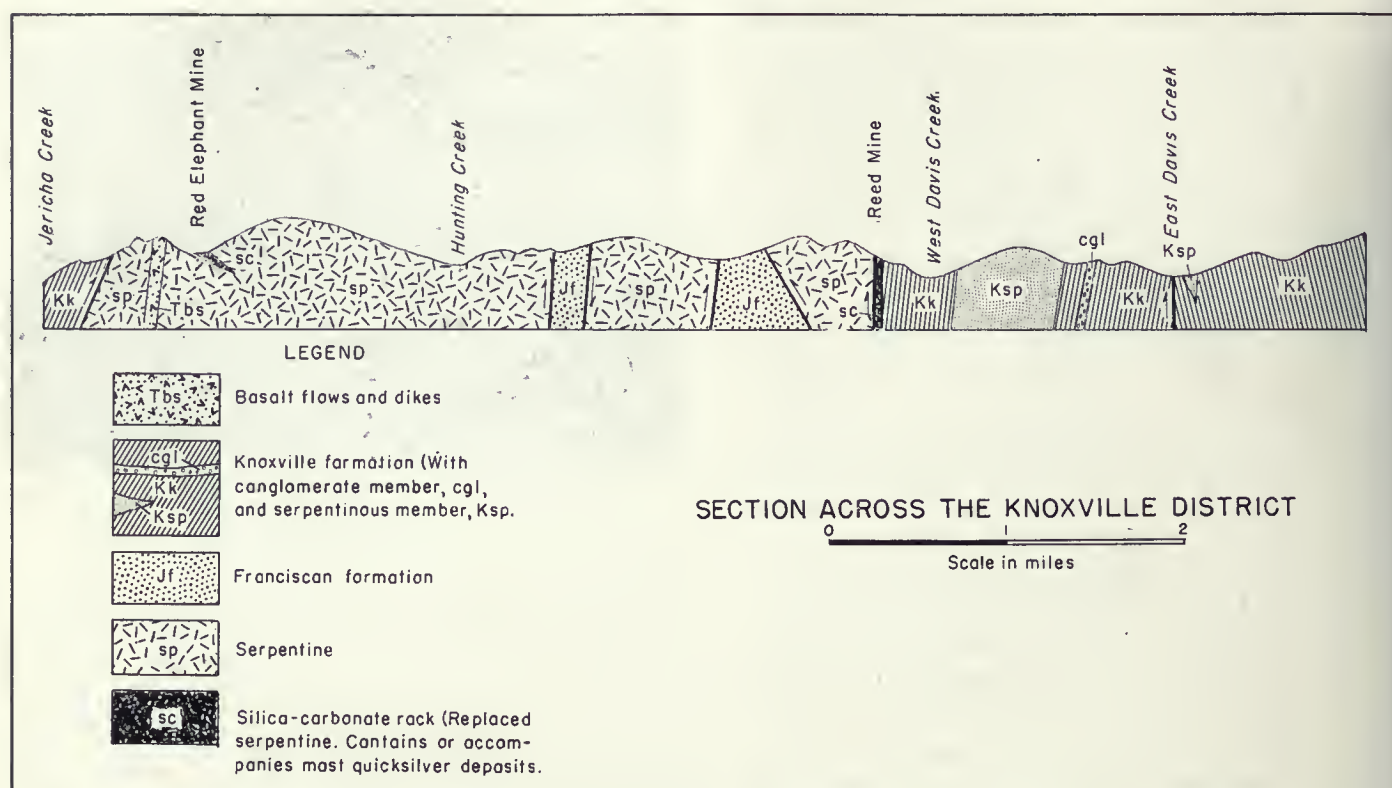


FIGURE 3. Geologic section across the Knoxville district, Lake, Napa, and Yolo Counties. After Averitt, 1945.

1939 bibliography on California mercury deposits has been provided by Ransome and Kellogg (1939) in a report which summarizes the salient features of most of the mines. During World War II many of the state's mercury-bearing areas were studied in detail by members of the U. S. Geological Survey. In recent years reports of these investigations have been published by the California Division of Mines: Knoxville district, Averitt 1945; Mayaemas district, Bailey 1946; Walibu mine, Bailey and Swinney 1947; New Idria district, Eckel and Myers 1946; New Almaden mine, Bailey 1951; Cachuma district, Skaggs Springs, Everhart 1950; Sulphur Bank mine, 1946; Oakville district, Fix and Swinney 1946; Guerneville district, Myers and Everhart 1948; Altoona mine, Swinney 1950; Panoche district, Yates and Hilpert 1945, Mayaemas district, 1946). Although the mercury deposits of the Coast Ranges province have formed under similar geologic conditions, they show marked differences in the character and grade of the ore and the nature of the gangue and host rock, as well as in the age of the host rock and size of the ore bodies.

The relatively few mercury mines in California that are outside of the Coast Ranges province are even less similar. The mercury deposits in the Diamond Creek area of Del Norte County are reported to occur as fissure fillings in altered diorite; and as replacements in felsite masses intruding sheared serpentine, (Cater and Wells, 1953). In the Beaver Creek area of Siskiyou County, cinnabar has been deposited as fracture fillings in metamorphic rocks. Cinnabar at the Altoona mine in northeastern Trinity County has been deposited in

narrow, steeply dipping "veins" along fault zones in porphyritic diorite (Swinney, 1950).

The Walibu (Cuddeback) mine, 10 miles northwest of Tehachapi in Kern County, is the southernmost of several mercury occurrences along the eastern flank of the Sierra Nevada. Here, mercury ore occurs in one of a number of rhyolite dikes which have intruded granitic rocks of the Sierra Nevada batholith. Cinnabar, the only mineral of economic importance, "energests fracture walls, fills small breccia veins . . . and is disseminated as minute crystals through the more altered rhyolite" (Bailey and Swinney, 1947).

Small amounts of quicksilver have been obtained from Recent hot spring deposits in the Coso district of southwestern Inyo County. The mercury deposits in this area consist of small irregular cinnabar veins in altered tuffs and altered granite. Silicification and kaolinization of the host rocks has been intense. In a deposit near Tustin, Orange County, cinnabar and native mercury are associated with small veins of barite in country rock of Tertiary sandstone.

**Mining and Treatment Methods.** As mercury deposits ordinarily occur in poorly defined and irregular zones that generally are parallel to or in fault zones, systematic exploration is difficult. Where cinnabar stringers cross the zone these are first explored by trenches and shallow underground workings. The occasional ore bodies that are thus encountered are worked by conventional stoping methods. The "heavy ground" which is characteristic of Coast Ranges mines requires substantial support, and square-set timbering is employed in large



stopes. Small, narrow ore shoots are worked by open stopes or stilled stopes. During World War II the shortage of miners encouraged installation of mechanical loaders, scraper hoists, and "jumbo" drilling equipment for drifting in the larger mines. Since mercury ore bodies are irregular and generally unpredictable in location, size, and grade, few deposits are adaptable to large scale shovel mining. Selective shovel mining has been employed successfully on a limited scale near old shallow underground workings, on dumps and as an aid to field up-grading of very low grade deposits.

The extraction of mercury from its ores is essentially a distillation process commonly referred to as "burning." Heating the ore in the presence of air oxidizes the sulfur and frees the contained mercury as a vapor, which condenses to the pure metal on cooling. The sulfur is discharged to the atmosphere as sulfur dioxide gas. Simple though the process may be in theory, many types of retorts, furnaces and condensers have been used with varying degrees of success. The ore is "burned" in two general ways. One method utilizes indirect heat and is similar to baking; the other utilizes direct heat and is termed "roasting."

In the "baking" method, cylindrical or semi-cylindrical iron tubes (retorts), placed horizontally or on a slant over brick fire boxes, are partly filled with ore crushed to minus 1-inch size. Each retort is sealed except for a vapor-outlet pipe in which condensation of mercury can take place. Retorting is a batch process and the operation follows a cycle of charging, heating, cooling, and withdrawal of burned ore. The use of retorts is most adaptable to a small mine producing high-grade ore that averages more than 1 percent mercury. Many retorts have successfully treated three charges, totalling about a ton of ore, per 24 hour day. As a retort can be easily constructed at small expense nearly every mine has its own refinery. Some small mines produce sufficient ore to operate a battery of retorts.

Greater ore capacity and efficiency with more continuous operation is gained in the various mechanical furnaces built to roast ore by direct heat. For this purpose, the horizontally inclined rotary furnace and the



FIGURE 5. Concentrating cinnabar sand by use of a rocker on James Creek, Napa County. James Creek receives drainage from the Oat Hill dump and other mines in the Eastern Mayacmas district.

stationary vertical furnace are now used almost universally. The Gould rotary kiln was installed first at New Idria in 1918. It revolves on a slightly inclined axis and the ore, crushed minus 2-inch size, usually moves, generally counter-currently, toward the heat source at the lower end. Nearly complete extraction of the mercury is accomplished, and the vapors are drawn off at the upper end through a cyclone dust collector. The flow of gases is stimulated by a suction fan. Mercury condenses from the vapor in banks of vertical pipes joined alternately at the top and bottom with U connections. Liquid mercury is collected under water which seals the hopper openings in the lower pipe connections.

The rotary kiln operates with increased fuel economy and overall efficiency compared to the older type of furnaces, and in addition eliminates most of the hazards of mercury poisoning which attended their operation. A much lower grade of ore can be profitably handled by a rotary furnace than by a retort. During World War II, when the price of mercury was about \$175 per flask, the feed to many rotary furnaces averaged a quarter of a percent mercury, or 5 pounds of mercury per ton of ore. During 1955 when the price of mercury was about \$270 per flask many potential operators were seeking large deposits of 3- to 4-pound ore.

The Nichols Herreshoff multiple hearth furnace has been successfully used to treat mercury ores. The furnace operates on a feed of minus 1½-inch size. It consists essentially of an upright cylinder having a number of horizontal hearths over which the ore passes in traveling from top to bottom of the furnace. Horizontal arms or rabblers attached to a rotating vertical shaft running through the center of the furnace, draw the ore toward openings through which it falls from hearth to hearth. Heated air and ore vapors are drawn through the furnace and delivered to the condensers by a counter-current blower system. This type of furnace is currently in use at the Cordero mine in Nevada.

**Marketing.** After liquid mercury is recovered from its ores by distillation, it is "bottled" and sent to market in a state of comparatively high purity known as "prime virgin." The U. S. Government in its mercury purchase



FIGURE 4. Looking eastward along Big Sulfur Creek toward the furnace plant of Buckman Mines near The Big Geysers, Western Mayacmas district, Sonoma County. Buckman Mines has been actively developing and producing from the former Culver Baer and Dewey mines during recent years.





FIGURE 6. New headframe at the Monnt Diablo mine, Contra Costa County. This construction was made in 1953 under the U.S. Government DMEA program for the exploration of domestic deposits. Ore bin is at right center.

program states that it will purchase "prime virgin mercury which is 99.9% chemically pure and is 'clean and bright.'" The product from mines in the United States ordinarily meets these requirements.

In the primary market the flask, consisting of 76 pounds of mercury, is the unit upon which all transactions are based. This quantity of mercury is packaged or "bottled" in a wrought iron or steel container known as a flask, and these containers can be purchased from the firms mentioned below at prices ranging from 50 cents to \$2 apiece, depending on the demand. The containers are used repeatedly and have been known to last more than 50 years in ordinary service.

**Buyers.** San Francisco by virtue of its industry and central location with respect to the mercury mines is the locus of the primary market. The large mercury producers, the principal industrial users and many mercury dealers maintain representatives in this city. Some of the mines are affiliated with chemical companies which use the entire mine output. The small mine lessees and partnerships usually sell their output to mercury dealers who in turn resell to their customers in industry. Some of the California firms who purchase mercury from mine operators are:

- F. W. Berk & Co., Coast Chemical Division  
55 New Montgomery St., San Francisco
- Braun Corporation  
2260 E. 15th St., Los Angeles
- Buckman Mines  
Geyser Road, Cloverdale
- Goldsmith Bros. Smelting and Refining Co.  
3918 Foothill Blvd., Oakland
- H. W. Gould & Co.  
Mills Bldg., San Francisco
- Los Angeles Chemical Co.  
1960 South Santa Fe Ave., Los Angeles
- Mefford Chemical Co.  
1026 Santa Fe Ave., Los Angeles
- Pacific Vegetable Oil Co.  
407 Sansome St., San Francisco
- Quicksilver Producers Association  
407 Sansome St., San Francisco
- U. S. Government, General Services Administration  
49 Fourth Street, San Francisco



FIGURE 7. Construction of a two-tube Rossi type ore-burning retort underway at the New Almaden property in Santa Clara County. Numerous groups of lessees are currently active at this mine.

Regulations governing the purchase by the U. S. Government of domestic and Mexican mercury for the national stockpile were announced July 6, 1954, by the General Services Administration. The program called for buying a maximum of 125,000 flasks of domestic mercury and 75,000 flasks of Mexican metal. Purchases are to be made until this amount has been obtained or until December 31, 1957, whichever occurs first. The price paid is to be \$225 per 76 lb. flask, f.o.b. delivery point, with duty paid by the vendor (\$19) in the case of the Mexican material.

Under the regulations, persons desiring to supply mercury were required to signify their intentions to do so in writing, or by telegram, to the Regional Director of General Services Administration, 49 Fourth Street, San Francisco, California.

A producer must notify the Regional Director at least 30 days in advance of an intention to ship. Prime virgin mercury which is 99.9 percent chemically pure and is "clean and bright" will be accepted in minimum lots of five flasks. While the wrought-iron or steel flask is standard, GSA may accept deliveries in other containers, of similar material, which are nominally the same size and shape. But all units in any given delivery must be in the same size and shaped containers.

Government inspectors will examine material arriving at the appropriate depots and will make the final decision as to whether or not the material meets specifications. Rejected shipments must be removed at the vendor's expense.

**Price.** The price per flask in New York is quoted weekly in the Engineering and Mining Journal Metal and Mineral Markets report, and this quotation is in turn based upon recent sales to consumers. During 1953 the price quoted in San Francisco by one prominent buyer ranged from \$4 to \$10 below the New York quotations for the same period. This differential covered the cost of freight to New York and handling charges such as insurance, local drayage, storage, and marketing profit. During the periods of rapidly rising prices between July 1950 and January 1951, and between March and October 1954 the San Francisco quotation often





FIGURE 8. Geologic section across Mine Hill, New Almaden mine, Santa Clara County. After Bailey, E. H., *California Div. Mines Special Rept. 17, pl. 1*.





FIGURE 9. Mining native mercury from ground underlying the old Knox brick furnace at the Guadalupe mine, Santa Clara County. The dragline feeds the washing plant where mercury and some cinnabar are recovered in Ainsley bowls.

exceeded the New York quotation. The Engineering and Mining Journal New York quotation of October 7, 1954, was \$325-\$330 per flask, an all-time high.

*History of Price and Production.* In 1824 the first recorded discovery of cinnabar in the United States was made in the hills south and west of San Jose, Santa Clara County, California. This locality later became the site of the famous New Almaden mine. The red mineral was not recognized as cinnabar and it was unsuccessfully treated for the recovery of silver. Twenty years passed before it was accurately identified. Mercury was successfully extracted about 1846 and a ready market for the metal was provided by the nearly simultaneous beginning of gold mining in the Sierra Nevada.

Mercury was essential to the placer miner in recovering gold from the pan, the rocker, and the sluice box. As the gold rush grew in importance so also did mercury mining. This trend was manifested by the increase in production from 7,723 flasks in 1850 to an all-time peak of 79,396 flasks in 1877. Much of this metal came from the very rich ore of the New Almaden deposit. In the years following 1850 many other deposits were found in various counties. The first recorded production at the Guadalupe mine was in 1857, the New Idria in 1858, the Knoxville in 1862, and the Aetna mines in 1864, the Great Western in 1873, the Sulphur Bank in 1874, and the Mt. Jackson (Great Eastern) in 1875.



FIGURE 10. Ledge of resiliified quartz breccia carrying meta-cinnabar and cinnabar cropping out at surface at Valley View mine, Panoche district, San Benito County. View northwest showing road, ore bin and ore chute from shallow underground workings.

Many other smaller mines contributed to the record production ranging from 50,000 to nearly 80,000 flasks per year during the years 1875-82 inclusive. The price fell rapidly from the \$105.18 average of 1874 to \$28.23 a flask in 1882, when a 10 percent ad valorem duty was placed on imports of mercury. It was a period of over-production despite the large consumption for gold amalgamation in hydraulic mining and in pan amalgamation at lode gold mines.

In the following years the duty on imported mercury was changed several times, but the price did not appreciably improve until World War I. An average price of \$114 per flask was reached in 1918, but by 1921 it had dropped to \$44.56. Following World War I the uncertainty of prices hindered development of the mines and reserves of ore were at a low point. The rich deposits of New Almaden appear to have been nearly exhausted before 1895, but moderate production continued until 1925.

In 1922 the duty was increased to \$19 per flask and, with growing industrial activity, a new impetus was given to mercury mining. The price reached an average of \$118.34 per flask in 1928, and a moderate gain in production was made up to 1931 when 13,478 flasks were recovered. Economic conditions forced the price down to \$52.30 in 1932. The New Idria mine was the principal source of mercury in California from 1895 until 1932 when operations were greatly curtailed by the depression and the belief that the mine was nearly exhausted.



FIGURE 11. Surface installations at the New Idria mine, San Benito County. This mine is California's largest current producer of mercury. Ore-crushing plant at left, kiln-house at right, camp in upper right background.

The start of Civil War in Spain and growing tension in Europe, however, created a shortage of mercury in the late thirties. Prices rose, mining was stimulated and production climbed from the low point of 4,102 flasks in 1933 to 33,948 flasks in 1943. The price reached \$184.58 (average) for 1942. In February 1942 a ceiling price of \$191 per flask f.o.b., shipping point, was placed on California mercury by the Federal Office of Price Administration. In the six-year period 1940 to 1945 inclusive, covering the duration of World War II, the price ranged from \$113.14 to \$184.58, averaging nearly



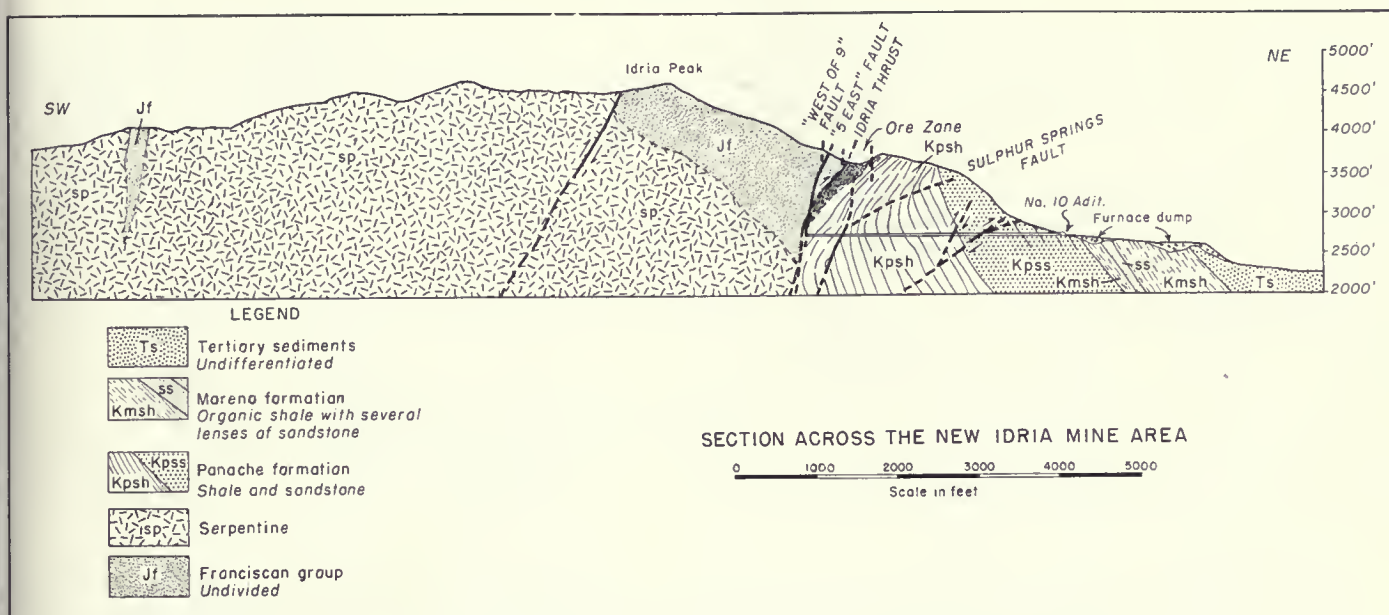


FIGURE 12. Geologic section across the New Idria mine. From Eckel, Yates, and Myers, 1946.

\$159.00 per flask at San Francisco. For the same period average production was 26,285 flasks per year.

Purchase contracts of the U. S. Government were cancelled in 1944. The price dropped, production declined, and this downward trend in domestic mercury production remained unchecked for 5 years.

After an initial post World War II slump, consumption continued at a higher rate than during any recent peace time period. Virtually all use-classifications shared in this increase, including construction of mercury boiler plants and the construction of chlorine and caustic soda plants which use mercury electrolytic cells. World supplies of mercury were more than ample in the post war period and the increased consumption was largely supplied by metal imported from low-cost mines in Spain, Italy and Yugoslavia.

The pertinent factors influencing the post-war mercury industry were: (1) large stocks of mercury here and abroad, (2) world production capacity at record height, (3) the extreme need of dollar credits by foreign countries, (4) the low production cost of Spanish, Italian, and other foreign producers.

A cartel, Mercurio Europeo, once controlled the marketing of both Spanish and Italian quicksilver. This organization later marketed only the Spanish output which is obtained principally from the fabulous Almaden Mines. The richness of the ore of Almaden exceeds by far any other mercury deposit in the world. With the added advantage of lower labor cost, Spanish mercury can be shipped to the United States, carry a \$19.00 per flask import tariff and still be profitably sold at a figure below domestic cost of production.

Low mercury prices accompanied by increased costs of mine operation resulted in the closing of nearly all the domestic mines. By 1950, California production had fallen to 3850 flasks, the lowest level in 28 years; and production in the United States fell to the lowest level in 100 years. Only one major domestic mine, the Mt. Jackson in Sonoma County, was in continuous operation

in 1950. In June of the same year the quoted price in New York had fallen to \$70-\$72 per flask.

The outbreak of war in Korea late in June 1950 resulted in a series of sharp advances in price which culminated in a New York quotation of \$225-\$227 per flask in January 1951. A few mines were reopened and production increased slightly during the next 2 years.

Under the Defense Production Act of 1950, mercury was classed as a strategic mineral, and mercury mines became eligible for U. S. Government exploration loans. Eight California mines received financial assistance: the Abbott, the Altoona, the Granada, the New Almaden, the New Idria, the Mt. Diablo, the Oceanic, and the Walibu. At New Almaden an unsuccessful drilling exploration program was begun in 1951 and completed in 1952. At New Idria an underground exploration program was begun in 1952 at the northwest end of the mine. This work proved successful and a new ore zone



FIGURE 13. Headframe and ore treatment plant at the Liouss Den mine, Cachuma district, Santa Barbara County. This mine was a producer during World War II.



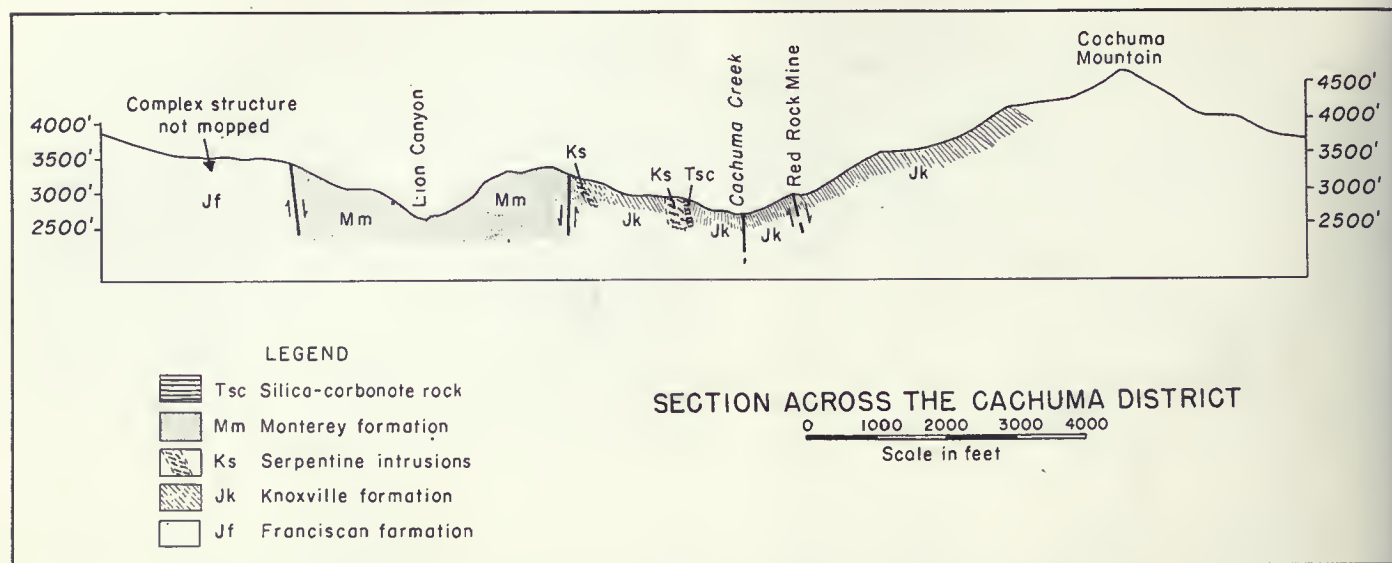


FIGURE 14. Geologic section across the Cachuma district, Santa Barbara County. *After Everhart, 1950.*

was found. Additional loans were granted in 1953 and 1955 to continue exploration in the West Idria and Molino areas. At Mt. Diablo an underground exploration program was begun late in 1953, was suspended during 1954, but was resumed in 1955 after a change in management at the mine; only small showings were discovered. The drilling program at the Walibu mine was unsuccessful. A large new ore body was developed under the government program at the Abbott mine. Exploration work at the Altoona mine did not begin until the latter part of 1955. Work is still in progress here as well as at the Granada and Oceanic mines.

The price of mercury hovered around the \$200 per flask level during the 3-year period January 1951 to January 1954. The price structure exhibited renewed vigor during the second quarter of 1954 and resumed its upward trend reaching an all-time peak of \$330 per flask in October 1954. The belief was widespread that federal purchases of mercury for use in the atomic energy program were reducing the available supply and were responsible for the increase in price during the year.

Meanwhile, on July 6, 1954, the General Services Administration announced a program for the purchase of

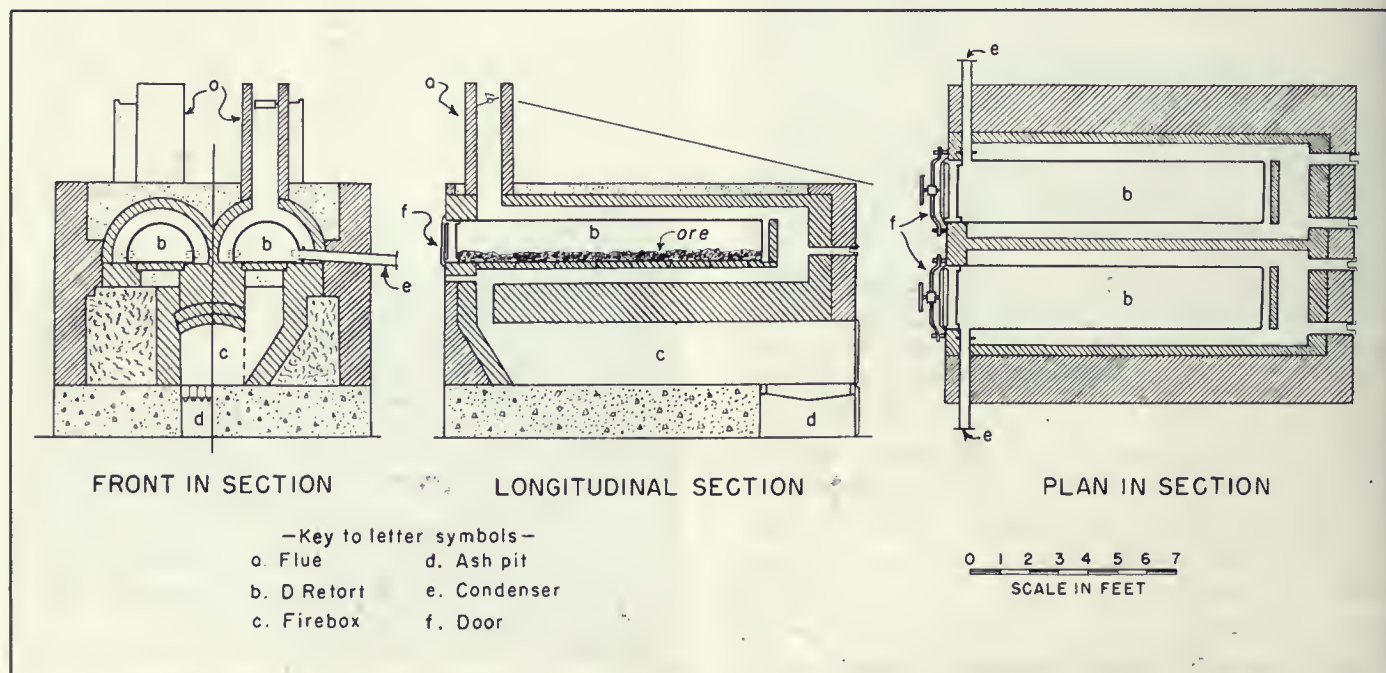


FIGURE 15. Details of a D-retort. *From U.S. Bur. Mines Inf. Circ. 6966.*



Table 1. Annual amount and value of mercury produced in California, 1850-1955.

(Flasks, as tabulated herein, contained 76½ lbs. from 1850 to May 1904, inclusive; 75 lbs. from June 1904 to 1927, inclusive; 76 lbs. from 1928 to date. Sources of information used in preparing this table are: 1850-83, a table by J. B. Rando published in

Report 4 of the State Mineralogist, p. 336; 1883-93, reports of the U. S. Geological Survey; 1894-1946, compiled by State Division of Mines; 1947-1955 compiled by U. S. Bur. Mines.

Year	Flasks	Value	Average price per flask	Year	Flasks	Value	Average price per flask
1850	7,723	\$768,052	\$99.45	1904	28,876	1,086,323	37.62
1851	27,779	1,859,248	66.93	1905	24,655	886,081	35.94
1852	20,000	1,166,600	58.33	1906	19,516	712,334	36.50
1853	22,284	1,235,648	55.45	1907	17,379	663,178	38.16
1854	30,004	1,663,722	55.45	1908	18,039	763,520	42.33
1855	33,000	1,767,150	53.55	1909	16,217	773,788	47.71
1856	30,000	1,549,500	51.65	1910	17,665	799,002	45.23
1857	28,204	1,374,381	48.73	1911	19,109	879,205	46.01
1858	31,000	1,482,730	47.83	1912	20,600	866,024	42.04
1859	13,000	820,690	63.13	1913	15,661	630,042	40.23
1860	10,000	535,500	53.55	1914	11,373	557,846	49.05
1861	35,000	1,471,750	42.05	1915	14,199	1,157,449	81.52
1862	42,000	1,526,700	36.35	1916	21,427	2,003,425	93.50
1863	40,531	1,705,544	42.08	1917	24,382	2,396,466	98.29
1864	47,489	2,179,745	45.90	1918	22,621	2,579,472	114.03
1865	53,000	2,432,700	45.90	1919	15,200	1,353,381	89.04
1866	46,550	2,473,202	53.13	1920	10,278	775,527	75.45
1867	47,000	2,157,300	45.90	1921	3,157	140,666	44.56
1868	47,728	2,190,715	45.90	1922	3,466	191,851	55.35
1869	33,811	1,551,925	45.90	1923	5,458	332,851	60.98
1870	30,077	1,725,818	57.38	1924	7,948	543,080	68.33
1871	31,686	1,999,387	63.10	1925	7,683	621,831	80.81
1872	31,621	2,084,773	65.93	1926	5,892	516,382	87.64
1873	27,642	2,220,482	80.33	1927	6,488	714,418	111.67
1874	27,756	2,919,376	105.18	1928	7,107	844,649	118.84
1875	50,250	4,228,538	84.15	1929	10,152	1,195,705	117.78
1876	75,074	3,303,256	44.00	1930	11,374	1,255,257	110.36
1877	79,396	2,961,471	37.30	1931	13,478	1,121,624	83.22
1878	63,880	2,101,652	32.90	1932	5,349	279,780	52.30
1879	73,684	2,194,674	29.85	1933	4,102	229,472	55.94
1880	59,926	1,857,706	31.00	1934	7,946	534,135	67.22
1881	60,851	1,815,185	29.83	1935	9,353	628,590	67.23
1882	52,732	1,488,624	28.23	1936	8,758	671,055	76.62
1883	46,725	1,343,344	28.75	1937	9,995	837,789	83.82
1884	31,913	973,347	30.50	1938	12,171	846,497	69.55
1885	32,073	986,245	30.75	1939	11,201	1,105,563	98.43
1886	29,981	1,064,326	35.50	1940	18,907	3,209,754	169.77
1887	33,760	1,430,749	42.38	1941	25,612	4,509,041	176.03
1888	33,250	1,413,125	42.50	1942	30,087	5,553,357	184.58
1889	26,464	1,190,880	45.00	1943	33,948	6,177,159	181.96
1890	22,926	1,203,615	52.50	1944	28,097	3,178,969	113.14
1891	22,904	1,036,406	45.25	1945	21,063	2,697,835	128.08
1892	27,993	1,139,595	40.71	1946	17,804	1,648,758	92.61
1893	30,164	1,108,527	36.75	1947	17,165	1,437,397	83.74 (NY)
1894	30,416	934,000	30.70	1948	11,188	855,770	76.49 (NY)
1895	36,104	1,337,131	37.04	1949	4,493	357,014	79.46 (NY)
1896	30,765	1,075,449	34.96	1950	3,850	313,000	81.26 (NY)
1897	26,691	993,445	37.28	1951	4,282	899,777	210.13 (NY)
1898	31,092	1,188,626	38.23	1952	7,241	1,441,683	199.10 (NY)
1899	29,454	1,405,045	47.70	1953	9,290	1,793,249	193.03 (NY)
1900	26,317	1,182,786	44.94	1954	11,262	2,977,560	264.39 (NY)
1901	26,720	1,285,014	48.46	1955	9,500	2,755,500	290.35 (NY)
1902	29,552	1,276,524	43.20				
1903	32,094	1,335,954	42.25				
				Totals	2,670,100	\$159,017,958	

125,000 flasks of domestic mercury by December 31, 1957 at the price of \$225 per flask. This announcement had the effect of establishing a floor price on domestic mercury for a 3½-year period and initiated a scramble for inactive deposits. By March 1, 1956, the open market price had declined to \$265 per flask. Only a token quantity of domestic mercury was purchased under the stockpile program during the first two years of its operation because the market price was at all times above the Government price. Domestic production, however, is increasing and the outlook for mercury mining appears favorable.

**Utilization.** The domestic consumption of mercury in 1954 (exclusive of possible unreported atomic energy uses) totaled 42,796 flasks. This total was distributed in generally recognized use categories as follows (U. S.

Bur. Mines, 1955): 33 percent in the manufacture of electrical apparatus, 21 percent in the manufacture of industrial and control instruments, 18 percent in agriculture, 7 percent in miscellaneous uses, 5 percent as dental mercury, 5 percent in electrolytic cells, 4 percent in pharmaceuticals, 3 percent in general laboratory use, 1 percent in catalysts, 1 percent in antifouling paint, ½ percent in amalgamation and ¼ percent in munitions. This distribution is shown graphically in the accompanying chart. These percentages vary from year to year, and many of the uses annually account for markedly different proportions of the total consumption in the United States.

Mercury is a metal which is obtained from its ores in a high state of purity. Since it is a liquid at ordinary temperatures it may be used where metallic properties are desirable, but where solid metals are unsuitable.



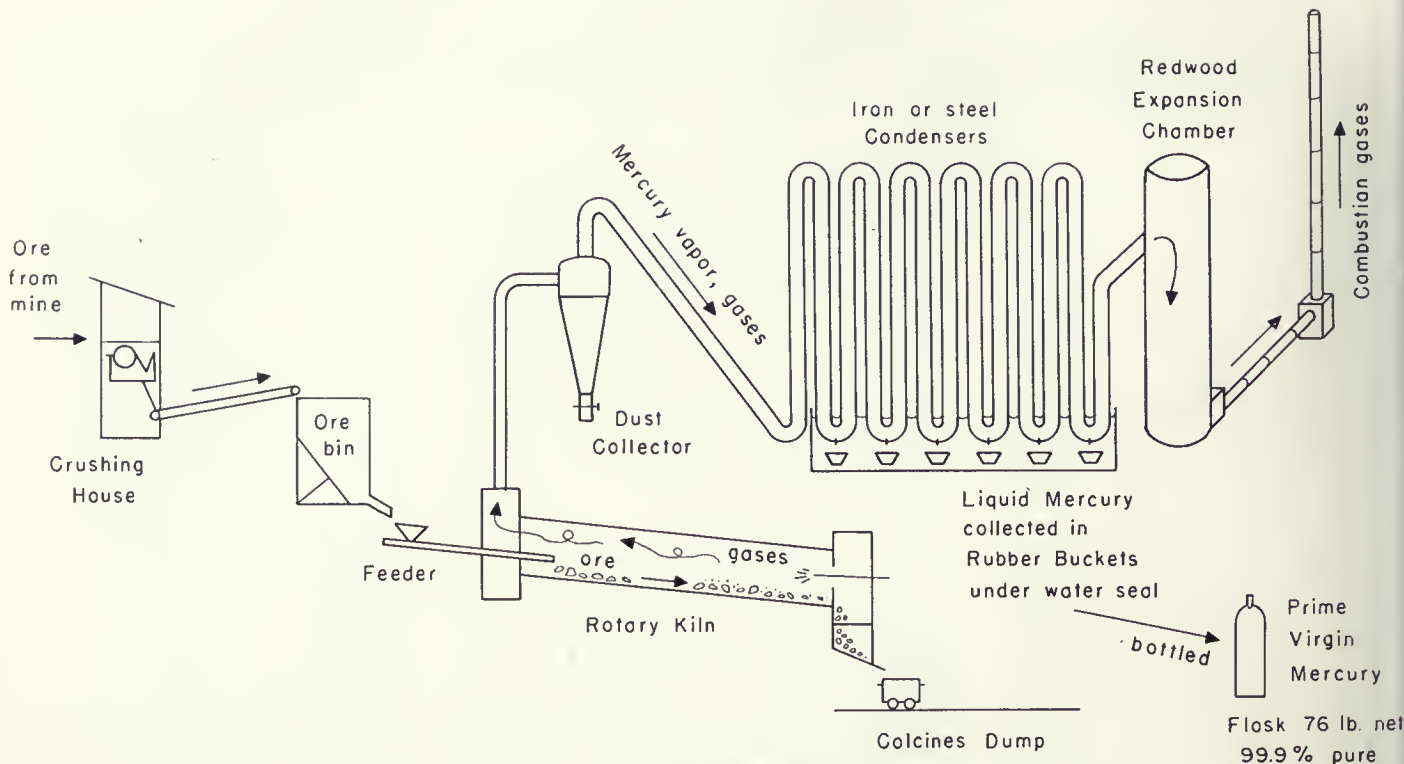


FIGURE 16. Typical flow sheet at a mercury mine.

The useful properties of mercury and the manner in which they are employed can be readily demonstrated by briefly reviewing the use categories mentioned above:

#### 1. Electrical apparatus.

As an excellent conductor of electricity, mercury is particularly useful in relay tubes, switches, rectifiers, oscillators, various vapor lamps, neon signs, and batteries.

#### 2. Industrial and control instruments.

The high density of mercury and its property as a conductor of heat are used effectively in thermometers, heat control devices, barometers, weightometers, gas-pressure gages, gas analysis apparatus, flow meters, compensating clock pendulums, vacuum pumps, gyrocompasses, and clutches.

#### 3. Agriculture.

As an important element in the manufacture of organic and inorganic compounds used in agriculture, mercury enters into the preparation of seed disinfectants, turf fungicides (ethyl mercury phosphate), and anti-septic plant germicides. Some of these are products used as a fungicide in the paper pulp industry (phenyl mercuric acetate), to prevent the formation of mold in paper pulp. They are used extensively in the paint and varnish industry both as preservatives and as fungicides. During the war they were applied as mildew rot preventatives for fabrics and leather.

#### 4. Dental Mercury.

Mercury is a good solvent for gold, silver, bismuth, cadmium, lead, sodium, tin and zinc; consequently it is easily contaminated. Solutions of silver, copper, tin, and zinc in mercury, known as amalgams, are used extensively as dental materials.

#### 5. Electrolytic cells.

The electrical conductivity and amalgamation of mercury are utilized in the electrolytic preparation of caustic soda and chlorine from a saline solution. At the mercury cathode a sodium amalgam is produced which immediately is converted into a caustic soda solution of high concentration and purity.

#### 6. Pharmaceuticals.

Inorganic compounds of mercury are known as mercury salts. Some inorganic compounds of mercury are poisonous and are used in medicine as antiseptics (mercuric chloride, mercury cyanide), as germicides (mercuric iodide), and as prophylactics. Many organic compounds such as phenyl mercuric acetate, a powerful germicide, are also pharmaceuticals.

#### 7. General laboratory.

Regulators, electrodes, pressure generators, liquid pistons, agitators and seals for water-soluble gases, are some of the devices employing mercury in general laboratory service.

#### 8. Catalysts.

Mercury salts are used in the manufacture of some organic compounds such as synthetic acetic acid.

#### 9. Antifouling paint.

Mercuric oxide is used in making paint for ship bottoms. Salt in the seawater converts the oxide to poisonous mercuric chloride which kills marine animals that attach themselves to the hull of the ship.

#### 10. Amalgamation (see 4 above).

The extraction of gold from its ores by amalgamation with mercury was once the principal use of mercury.



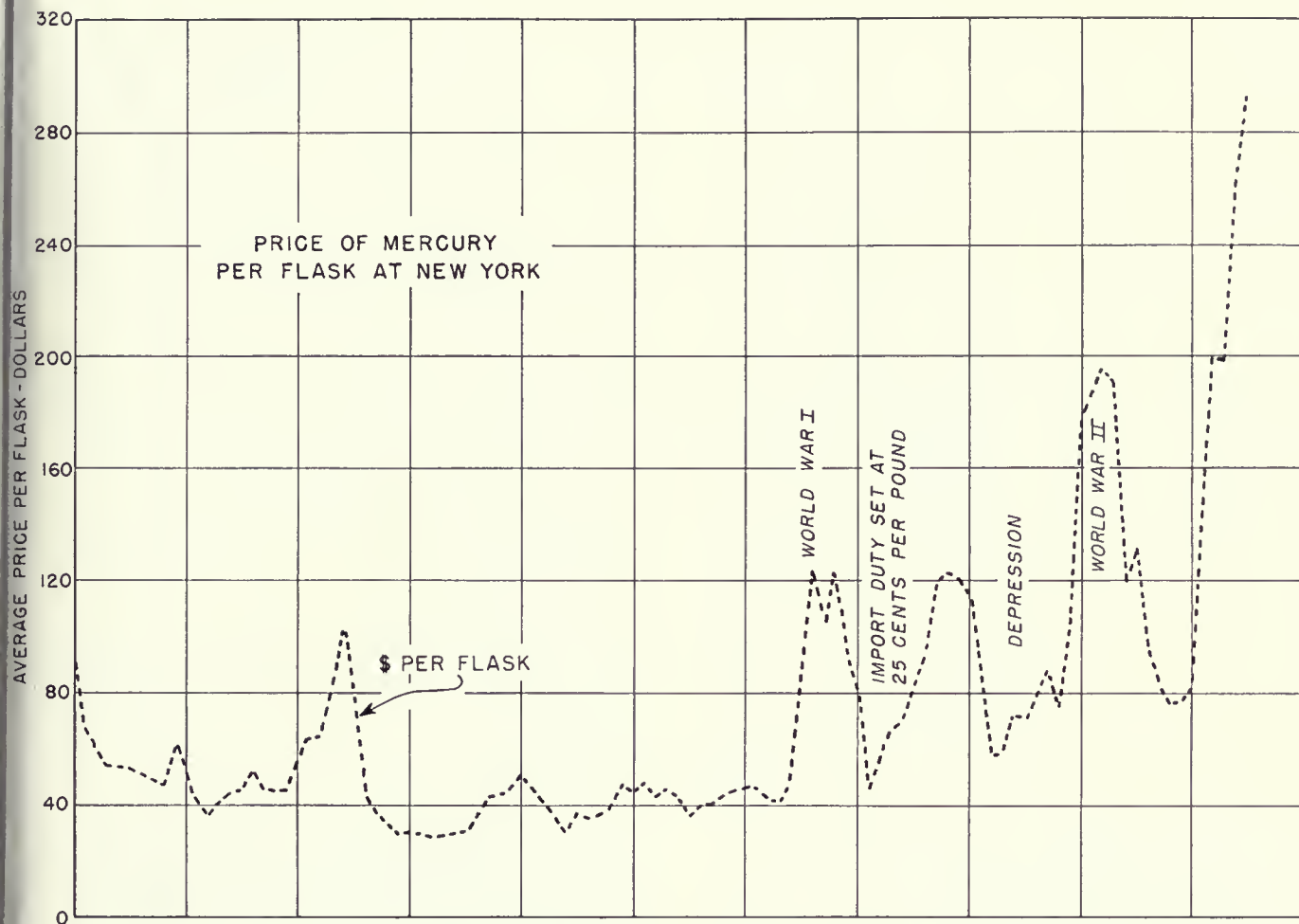


FIGURE 17. Chart showing price of mercury, 1850-1955.

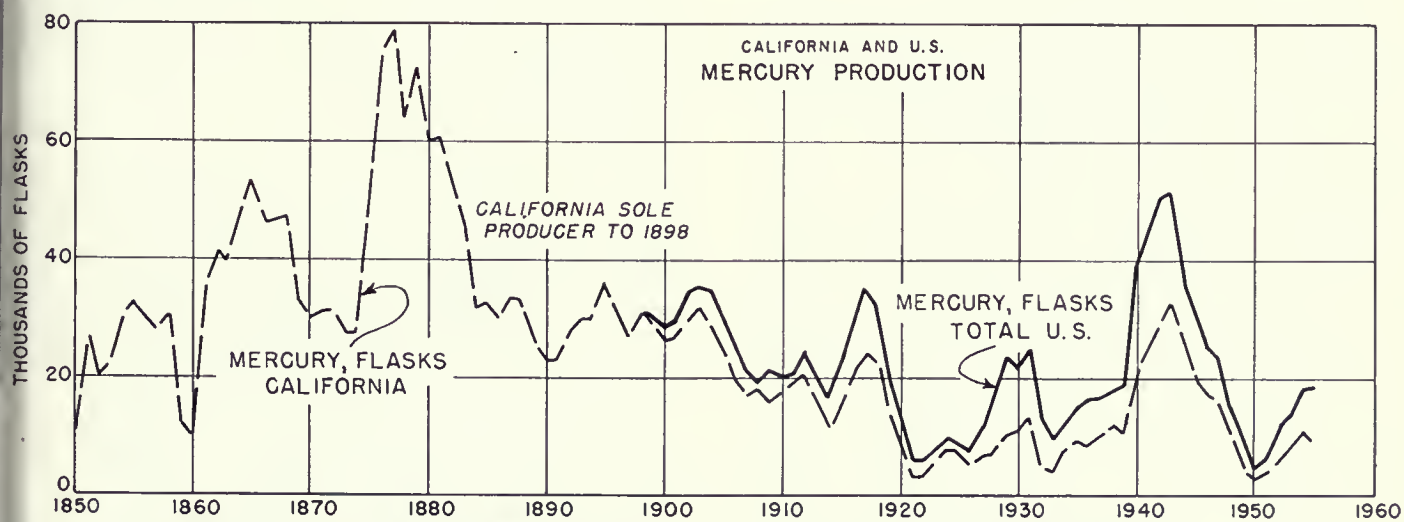
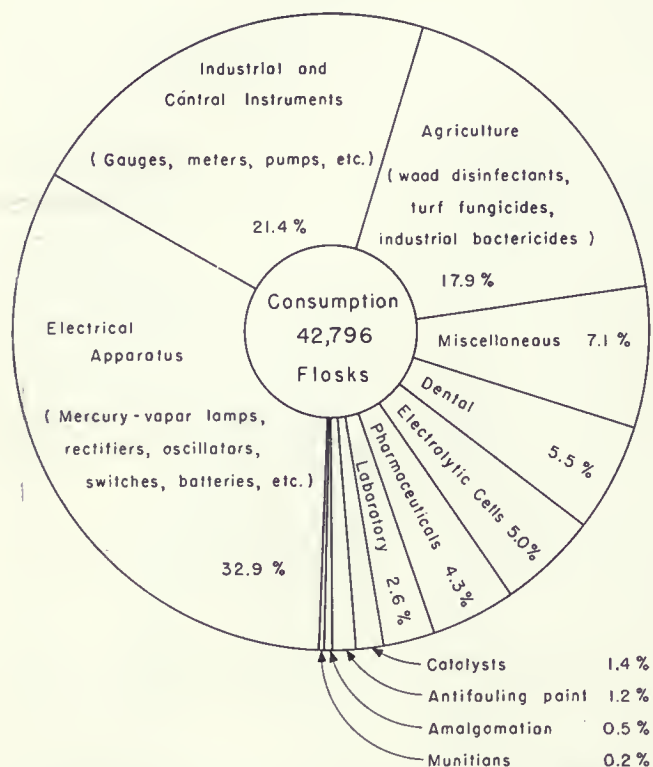


FIGURE 18. Chart showing production of mercury in California and the United States, 1850-1955.



## CONSUMPTION OF MERCURY IN THE UNITED STATES.

1954



U. S. Bureau Mines 1955, Mercury in 1954: Mineral Market Report MMS 2443.

FIGURE 19. Chart showing principal uses of mercury in the United States during 1954.

The consumption for this purpose is now at a very low level because of the small amount of gold being mined in the United States.

## 11. Munitions.

Some compounds of mercury are explosive. In the past, large quantities of mercury were consumed in the production of mercury fulminate for use as a detonator in munitions and blasting caps. Several other materials are now being substituted for mercury fulminate and its use is diminishing, except in time of war.

## 12. Power Generators.

Among the miscellaneous industrial applications of mercury is its use in steam power generation. This system combines the mercury-vapor cycle with the steam cycle to produce power from fuel with a thermal efficiency far greater than possible from the steam cycle alone. The essential equipment includes a mercury boiler in which mercury is vaporized and conducted through a turbine to generate electricity. The mercury vapor is then condensed and the heat evolved is used to convert water to steam for the operation of a steam turbine electric-generator. The application is most effective in areas deficient in sources of hydro-electric power and low-cost fuels.

## Utilization in California.

The consumption of prime virgin mercury in California is estimated to be about 10 percent of the national total, or a maximum of 5,000 flasks per year. This is roughly equal to about half the current California production.

The principal industrial outlet for prime virgin mercury produced in California is to manufacturers of mercurials, mercury salts, pharmaceuticals, agricultural products, and instruments, whose plants are located outside the state. A large quantity of these manufactured products are returned to California and distributed widely throughout the state. An important quantity of prime virgin mercury produced in California is consumed locally in the preparation of red mercuric oxide which is sold to California paint companies and used in the manufacture of antifouling paint. A small quantity of prime virgin mercury is consumed in California in the maintenance of industrial instruments such as flow meters, and in the manufacture of electronic devices. Some prime virgin mercury is used also in gold mining in California to recover gold and silver from the ore of the lode mines, and from gravels on the dredges and in other placer mines.

*Industrial Specifications.* Many descriptive names are used in industry in an attempt to designate the various grades of mercury which are available in the ordinary channels of trade. These names may be divided into two classes: those that mean something and those that do not.

Such titles as Technical, CP (Chemically Pure), Triple Distilled, and Cathodic, while they may imply the method of manufacture, give no hint as to the actual purity of the product. On the other hand such designations as ACS, NF, ADA, and USP indicate that a product meets certain specifications publicly available and publicly accepted for certain uses.

Impurities of mercury are of two kinds: undissolved foreign matter (dirt, rust or scale from flasks, oil, water, etc.) which floats on the mercury and can be removed by simple filtration; and dissolved impurities (usually metals) which render the mercury less fluid and impart other undesirable effects. Usually these impurities are detected by examining the appearance and the residue after ignition.

Some of the "public specifications" of common knowledge are listed in the accompanying table 2.

As can be seen there is a vast range in the allowable residue on ignition. Rather than market these grades individually, a manufacturer may select the various grades which can be produced in commercial quantities in accordance with good commercial practice, give each grade a trade name and then show on his labels the specification that the mercury meets. Grades of mercury for sale by one large manufacturer of mercury products are shown in the accompanying table 3.

Other firms label mercury as "Special Instrument grade," "Precision tube mercury," etc. Some firms use "Redistilled." Thus, fundamentally, there are really only four commercial grades, Prime Virgin, ADA, NF IX, and ACS because only these grades are defined in terms of specifications which are publicly available.



Table 2.

	Appearance	Residue on ignition
ACS (American Chemical Society)-----	Bright, free from scum	0.0005%
NF IX (National Formulary)-----	Bright, globular	0.01%
ADA (American Dental Association)-----	" , mirrorlike	0.02%
Military Specifications:		
MIL-M-191A & B-Grade I -----	" , " , free from scum	0.10%
" " -Grade II -----	" , " ,	0.005%
Veterans Administration-VA-D-23-----	" , " ,	0.02%
USP (U. S. Pharmacopeia) This is obsolete and not brought up to date.		

Table 3.

Prime Virgin	Mercury as it comes from the mines, 99.9 percent pure. Meets MIL-M-191A Grade I. Only available in iron flasks, 76 lbs. net. No label.
Technical	Prime Virgin cleaned and filtered and repacked into 10, 5, and 1 lb. jugs. It is not "redistilled" or "triple distilled." Meets MIL-M-191A, Grade I specification. No analysis is shown on the label.
Cleaned Virgin	"Triple distilled" or "redistilled" mercury meeting NF IX, ADA, MIL-M-191A Grade II, and VA-D-23 specifications. Only available in lacquer-lined iron flasks, 76 lbs. net. No label (guaranteed "triple distilled" NF IX quality when packed).
Triple Distilled	Meets NF IX, MIL-M-191A Grade II, and VA-D-23 specifications. Only available in 10, 5, 1 lb. bottles or jugs.
<p style="text-align: center;"><i>Label analysis</i></p> <p style="text-align: center;">Maximum impurities—Conforms to NF and ADA Specifications</p>	
	Non-volatile -----0.001%
	Insoluble in HNO <sub>3</sub> -----0.000%
	Base metals -----0.00%
Reagent Cathodic	Meets ACS specifications. Only available in 10, 5, 1 lb. bottles or jugs.
<p style="text-align: center;"><i>Label analysis</i></p> <p style="text-align: center;">Maximum impurities—Conforms to ACS Specifications</p>	
	Non-volatile matter -----0.0000%
	Insoluble matter -----0.0000%
	Foreign matter -----0.0000%

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## MICA

### Muscovite, Mica Schist, Vermiculite and Biotite

By LAUREN A. WRIGHT

Although coarse-grained muscovite mica occurs in pegmatite bodies in California, none of these deposits has become a continuing and profitable source of muscovite of any commercial grade. Flake mica, however, has been obtained locally in California from extensive occurrences of mica schist. Such material has been quarried near Ogilby, Imperial County, since the late 1920's and for shorter periods from deposits in southern Mariposa County, and near Hodge, San Bernardino County. Sericite-rich materials are mined in the Victorville-Barstow area of San Bernardino County and in the White Mountains of Mono County.

Sheet muscovite, which is unflawed and hence suited to use in electrical equipment, is a strategic material in which the United States is not self-sufficient. Recent progress in the development of synthetic muscovite, however, may lead to an alleviation of this shortage. In California, little or no market exists for unfabricated sheet mica, although large quantities of mica-bearing parts for electronic equipment are shipped into the state by eastern manufacturers. Each year several thousand tons of ground scrap mica are marketed in California, mainly for use as a paint extender. This is obtained mostly from deposits in India and the southeastern United States. The mica schist that is mined in California is used mostly as a lubricant for roll roofing.

Vermiculite, an expansible mica which is employed as an insulating material and light-weight aggregate, is brought into California from Idaho and from the Union of South Africa. It is expanded at plants in the Los Angeles and Sacramento areas.

*Mineralogy and Geology.* "Mica" is a general term for a group of aluminum silicate minerals with nearly perfect basal cleavage which permits them to be split into thin sheets. Such sheets, when bent, are tough, flexible, and elastic—properties that distinguish the micas from other minerals that they otherwise resemble.

Muscovite ( $\text{H}_2\text{KAl}_3(\text{SiO}_4)_3$ ), the so-called "white mica" is by far the most abundant mica of commerce and is the mineral ordinarily implied in the commercial use of the group name. Fine-grained muscovite is termed sericite. Phlogopite ( $(\text{H},\text{K},\text{Mg},\text{F})_3\text{MgAl}(\text{SiO}_4)_3$ ) closely resembles muscovite and is used for some of the same purposes, but in very few localities does it form deposits of commercial interest. Biotite ( $(\text{H},\text{K})_2(\text{Mg},\text{Fe})_2\text{Al}_2\text{SiO}_4$ ), or "black mica," is very common, but of little economic value. Vermiculite ( $(\text{OH})_2(\text{Mg},\text{Fe})_3(\text{Si},\text{Al})_4\text{O}_{10}\cdot 4\text{H}_2\text{O}$ , an expansible mica, is a low-cost material used mostly as an insulating material and as a light-weight aggregate. Lepidolite ( $\text{K},\text{Li}(\text{Al}(\text{OH},\text{F})_2)$ ) and innwaldite ( $(\text{K},\text{Li})_3\text{FeAl}_3\text{Si}_5\text{O}_{16}(\text{OH},\text{F})_2$ ) are commercial sources of lithium (see section on lithium in this volume) and roscoelite ( $\text{H}_8\text{K}(\text{Mg},\text{Fe})(\text{Al},\text{V})_4(\text{SiO}_3)_{12}$ ) as been an ore of vanadium.

Muscovite is common in most bodies of granitic rocks and in many bodies of metamorphic and sedimentary rocks, but only an exceedingly small proportion of these occurrences constitutes economic sources of muscovite.

Coarse-grained muscovite is restricted to pegmatite bodies and even in these, muscovite concentrations that are large enough and rich enough to have been profitably mined are uncommon except in a relatively few districts. Such concentrations ordinarily occur in zoned rather than unzoned pegmatite bodies, and generally are related in space to the zonal structures. In some pegmatites the muscovite has formed largely or wholly as a primary mineral during the initial consolidation of the rock, but in other pegmatites, it also occurs with albite in bodies that have replaced parts of the original zones. In some pegmatites individual zones are uniformly muscovite-rich and can be mined in their entirety through lateral and vertical distances of several hundred feet, but muscovite concentrations of commercial interest ordinarily occur as plunging shoots within individual zones or along the contacts between zones. Most of the productive shoots have contained 10 percent to 15 percent muscovite, and some are many tens of feet long.

The muscovite obtained from such deposits consists of "books" that range from a small fraction of an inch to several inches or even several feet in diameter. The mined product is divided on the basis of quality into (1) "sheet mica" which is clear, flat, and free enough from defects to be suited for shaping into items that are used in certain appliances, especially electrical equipment, stoves, and lamps; and (2) "scrap mica" which consists of pieces too small or too defective to be used as sheet mica.

Only an estimated 2 to 3 percent of the total volume of muscovite removed from the typical sheet mica-bearing pegmatite is ultimately sorted out and sold as sheet mica. The recovery of sheet mica is most hindered by the existence of structural imperfections in the mica crystals, and the most common of these are "reeves" which are minute striations or narrow folds in the plane of cleavage; "wedging" in which complex structures are caused by the interlayering of sheets of unequal size; "warping" which is characterized by ribs and ripples that are larger and more widely spaced than reeves; and "ruling" which consists of well-defined parting planes at an angle of nearly  $67^\circ$  with the cleavage plane (Jahns and Lancaster, 1950). Sheet mica also is reduced in value by the existence of tiny gas bubbles, inclusions and intergrowths of other minerals, and coatings or staining by secondary minerals and organic materials.

The profitable removal of mica concentrations in many pegmatites depends largely upon the proportion of recoverable sheet mica that they contain. Some pegmatite districts, including those in California, contain virtually no sheet mica, whereas the mica output of some of the deposits in North Carolina has contained as much as 10 percent sheet mica. In the United States a relatively small proportion of the pegmatite operations has been worked successfully on scrap muscovite alone.

The world's most productive muscovite districts are in India and Brazil, where mica-bearing pegmatites are very numerous. Although not extraordinarily rich or



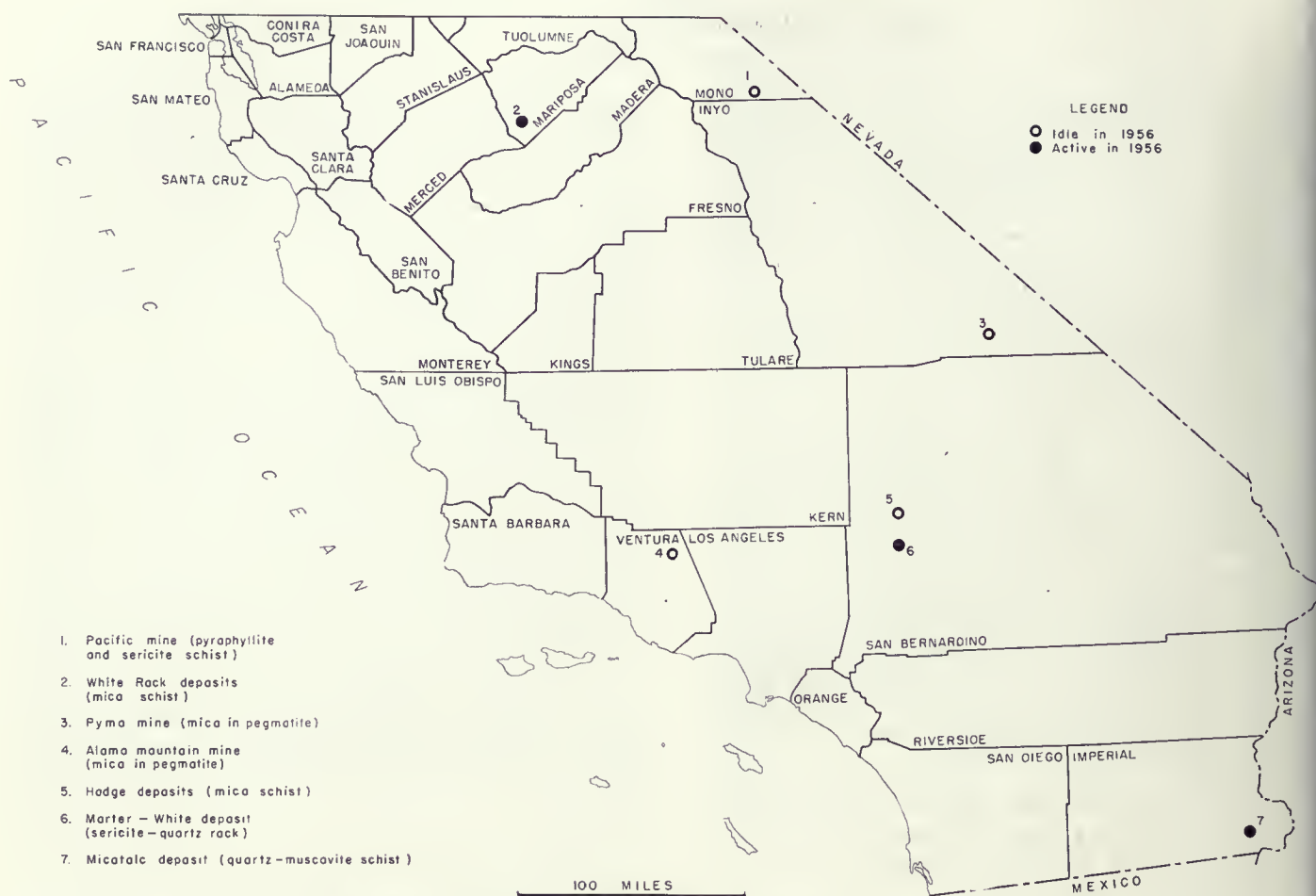


FIGURE 1. Index map of southern part of California showing locations of mica operations.

large, the deposits have been extensively developed by cheap labor. Since the end of World War II these and other foreign sources have supplied all but a small fraction of the sheet mica consumed in the United States (Dietrich and Thomson, 1955, p. 9).

Considerably more than one-half of the mica produced in the United States has been obtained from a pegmatite district that extends from central Virginia southward to central Alabama and centers in North Carolina (Jahns and Lancaster, 1950; Jahns, Griffiths, and Heinrich, 1952). Within this area muscovite-bearing pegmatites and larger bodies of other silicic rocks, all probably of late Paleozoic age, are intrusive mostly into pre-Cambrian (?) metamorphic rocks. Nearly 5,000 of the pegmatites have been mined or seriously prospected, and many of them were opened in the period 1875 to 1900. From 1914 to 1955 the district yielded about 31 million pounds of sheet muscovite, much of which was obtained from several hundred small, part-time operations. The other muscovite-bearing pegmatites of commercial interest in the United States are widely scattered, but most of them are in New England (Cameron et al., 1954) and South Dakota (Page et al., 1953). In 1956, the nearest of the actively worked sources of scrap mica to California, was the Capitan mine in the Petaca district of northern New Mexico (Jahns, 1946, p. 190). Here,

mica-bearing pegmatite was being mined, beneficiated and ground by the Petaca Mica Company, Santa Fe.

The mica schists of the world contain an incomparably greater volume of muscovite than do pegmatites. In the schists, however, the muscovite is much finer grained and is intimately mixed with other minerals, principally quartz and feldspar. When ground, the schist is called "flake mica" as distinguished from scrap mica which is purer. In general, the mica schists that are mined are parts of very extensive terranes of metamorphic rocks and are available in very large tonnages. The mined deposits, which are very few, ordinarily contain at least 10 percent mica and are near industrial centers.

Large quantities of phlogopite of both sheet and scrap grade are brought into the United States, principally from sources in Ontario and Quebec, Canada, and in Madagascar, but the mineral has not been mined domestically. Phlogopite of commercial grade occurs in highly metamorphosed sedimentary rocks that have been intimately invaded by granitic bodies and is generally believed to be a product of metamorphism. The Canadian deposits are associated with pyroxenite and occur as irregular shoots or veins that appear to have filled cavities or fissures. They have been developed by numerous shallow workings (Spence, 1929).

Although the vermiculite deposits of the world have been incompletely studied, most or all of the deposits



of commercial interest appear to be hydrothermal alterations of ultrabasic rocks. Such an origin has been ascribed to the vermiculite deposits near Libby, Montana, which are the principal domestic source. These deposits contain many millions of tons of rock bearing 30 to 95 percent vermiculite (North and Chandler 1953) and supply most of the vermiculite consumed in California.

*Localities in California.* Although pegmatites are numerous in California, particularly in the Peninsular Ranges province of Riverside and San Diego Counties, none of them has been operated profitably as a source of either sheet or scrap mica and most of them are virtually barren of such material. Even the most micaceous parts of the mica-bearing pegmatites generally average only a few percent muscovite, and this ordinarily is flawed by structural imperfections, especially by reeves and wedging, and, to a lesser extent, by ruling and mineral inclusions.

All of the recorded production of muscovite from pegmatites in California has been obtained from two very small operations—at Alamo Mountain in northeastern Ventura County and at the Pegma mine in the southern Death Valley area of Inyo County. The mica property at Alamo Mountain was active during the period 1902-04, but has since been idle. The deposit occurs in a pre-Cretaceous crystalline complex, and has been described as a muscovite mica "in a feldspar gangue, between a granite hanging and a mica schist footwall" (Aubury, 1906, p. 27; and Huguenin, 1919, p. 763). Most of the mica output was ground at a small mill near Piru Creek and was marketed for use as a lubricant and as a filler in the manufacture of roofing, wall paper, and rubber. Several hundred pounds of small books of sheet mica are said to have been used in the fabrication of washers and electrical insulators.

The pegmatite at the Pegma mine is part of the earlier pre-Cambrian complex that is extensively exposed in the central and southern parts of the Black Mountains in east-central Inyo County. In the late 1940's and early 1950's several hundred tons of scrap mica were removed from shallow surface and underground workings. In a 20-ton mill on the property, the mica was sent through an impact mill, a cyclone collector and vibrating screens. It was bagged in sizes that ranged from plus 20 mesh to minus 200 mesh (Norman and Stewart, 1951, p. 103).

The mica schist property near Ogilby, commonly known as the Micatale deposit, is in the pre-Cambrian Vitrefrax formation that also includes the Ogilby kyanite deposit described elsewhere in this volume. This formation is exposed in a belt, about a mile long, on the west flank of the Cargo Muehacho Mountains (Henshaw, 1942). Most of the mica schist is in discontinuous bodies as much as 100 feet thick and several hundred feet long. The rock is essentially a medium-grained mixture of muscovite and quartz.

Since the Micatale deposit was first worked in 1929, it has been in nearly continuous operation and had yielded several tens of thousands of tons of flake mica through 1955. The mica schist has been obtained from several closely spaced quarries, and is sent through a 72-ton mill which contains a jaw crusher, a Sturtevant mechanical separator and Rotex screens. It has been used almost

wholly as a lubricating dust for the surfaces of rolled roofing and is mined, milled and marketed by the Western Non-Metallies, 109 North Vineland, Puente.

In Mariposa County, muscovite-quartz schist has been mined in the White Rock district about 13 miles southwest of Mariposa. The schist is metamorphosed rhyolite tuff of the Cosumnes member of the Upper Jurassic Amador group (Bowen, 1957). It is very abundant, but the proportion of contained commercial material is undetermined. During the period 1937-43, several thousand tons of material were removed from the quarry and ground and screened at LeGrand, Merced County. The product is said to have been marketed as a lubricant in the manufacture of automobile tires.

The mica schist deposits near Hodge in San Bernardino County are part of the Upper Paleozoic Hodge volcanic series (Bowen, 1954, pp. 151-152), and form steeply dipping tabular masses in other metavolcanic rocks. Some of the schist is composed almost wholly of muscovite, but most of it contains quartz in various proportions. The schist was quarried during the early 1940's when 1,000 or more tons was removed and milled by Kennedy Minerals Company of Los Angeles.

In Mono County, mica schist, which is said to consist almost wholly of sericite, has been quarried at the Pacific pyrophyllite mine of Huntley Industrial Minerals, Inc. It occurs in layers adjacent to the pyrophyllite deposit (see section on pyrophyllite in this volume).

An exceedingly fine-grained mixture of sericite and quartz, known by the trade name of Marter-White and quarried between Victorville and Barstow in San Bernardino County, can be broadly classified as mica. In its physical properties and uses, however, it is more closely allied with clay or pyrophyllite. The material occurs in several hydrothermally altered zones in volcanic rocks of the Mesozoic Sidewinder series (Bowen, 1954, p. 154-158; Pask and Bowen, 1954). Several tens of thousands of tons have been mined, and the reserves apparently are many times larger. The rock is used as an extender and filler mostly in asphalt-type coatings, and in battery casings and other hard rubber objects.

Each year a small tonnage of biotite concentrates is marketed by Del Monte Properties Company as a by-product of the magnetic treatment of beach sand at Pacific Grove. The biotite is marketed, as flake mica, mainly as a lubricating agent for roll roofing surfaces.

No vermiculite or phlogopite has been mined commercially in California, but a vermiculite occurrence at the Asbestos King mine, about 15 miles southeast of Indio, Riverside County, has been seriously prospected.

*Mining Methods, Treatment, and Classification.* Most of the sheet and scrap muscovite that is mined in the world, is removed by means of small, laboriously worked underground mines. In the United States, these rarely exceed 300 feet in depth. Some pegmatite mica and virtually all of the mica schist as well as all of vermiculite mined in the United States are quarried.

The preparation of sheet mica for use by fabricators is done entirely by skilled hand-labor and involves a grading classification and terminology that are perhaps the most complex of any mineral commodity. In brief, this process consists of (1) clobbering impurities and defective mica from "mine-run" or "book" mica; (2)



roughly splitting and trimming by means of fingers; (3) further splitting and trimming with a blade to remove the major defects; and (4) classification of each sheet according to size, degree of trimming and quality. After classification most sheet mica is further split and knife-dressed before it is fabricated.

The term "block" mica commonly is applied to regularly shaped sheets at least  $1\frac{1}{2}$  by 2 inches on a side and 0.007 or more inches thick. High quality mica split to specified thicknesses in the range of 0.0012 to 0.004 inches is known as "film" mica. Material that is smaller than block, is termed "punch" mica if it can yield sheets  $1\frac{1}{2}$  inches in diameter and "washer" mica if pieces one inch in diameter can be produced. "Circle" mica can be trimmed to sheets 2 inches in diameter.

Nearly three-fourths (10.3 million pounds in 1953) of the sheet mica consumed in the United States are known as "splittings" and consist of lower quality pieces with a maximum thickness of 0.0012 inches. As splittings can be profitably produced only by cheap labor, they are obtained only from foreign sources, principally India.

Block and film mica are graded according to the sizes of the largest usable rectangles that can be cut or stamped from single sheets, and are classified quality-wise by the recognition of physical defects either by visual inspection or by a combination of visual inspection and electrical testing (Jahns and Lancaster, 1950; Dietrich and Thompson; American Society for Testing Materials, 1952 and 1953; Dietrich and Thompson, 1955; and Thompson, 1955 and 1956).

Serap and flake mica are prepared for market either by dry- or wet-grinding methods. The mill feeds for most serap mica grinding operations range in mica content from about 75 percent for material to be used in roofing to 98 or more percent for the highest quality grades. The purest feed consists of rejected mica from trimming shops, and its availability is tied directly to variations in the activity of sheet mica mining. Most ground mica, however, originates as ordinary serap, and most of this requires beneficiation before grinding. The up-grading of serap mica has been attempted in numerous ways, but the only widely used method consists merely of successive crushing and screening. Fragments of most minerals and rocks pass through screen openings much more easily than mica.

The dry-grinding ordinarily is done in high-speed hammer mills or disintegrators from which the mica passes to rotary or vibrating screens to yield products that range from 8 mesh to 100 mesh. The material from the Micatale deposit near Ogilby, Imperial County, is milled in this manner. At another dry-grinding mill, the Los Nietos plant of the Sunshine Mica Company, 440 Seaton St., Los Angeles, serap mica brought in from the southeastern United States and India is milled.

In the most common wet-grinding process, a batch of mica is fed into a chaser mill in which wooden rollers rotate in wooden or wood-lined tanks. Water is added and, after a several-hour grinding period, the charge is removed, dried, screened and bolted to sizes that range from 160 to 325-mesh. Although wet-grinding is more expensive and time-consuming than dry-grinding, it yields a purer product with a higher sheen. No wet-grinding mica mills exist in California.

The mica schist that is mined at the Pacific pyrophyllite quarry, Mono County, is ground to 99.5 percent minus 325-mesh in a Raymond mill at Laws, Inyo County, in the same manner as tale and pyrophyllite (see corresponding sections). The Marter-White material is ground, also to 99.5 percent minus 325-mesh, at a similar mill by the Southern California Minerals Company in Los Angeles.

The vermiculite-bearing rock, mined at the Libby, Montana, deposit, is screened and the waste removed as plus 2-inch oversize. The minus 2-inch material is briefly heated in rotary kilns to remove the free water; and next screened and passed through a crusher so that the hard impurities may be pulverized and removed. The concentrates are then shipped to widely distributed exfoliating plants. The exfoliation yields a product that generally is 8 to 12 times the volume of the unexpanded material. The expansion is accomplished in vertical shaft furnaces, usually at temperatures of 1,600 degrees F. to 2,000 degrees F., in a period of 4 to 8 seconds. The product is then screened to sizes that range from  $\frac{1}{4}$  inch-20 mesh, to minus 270 mesh.

In 1956, three plants in California were engaged in exfoliating vermiculite—two operated by the California Zonolite Company (5440 San Fernando Road, Los Angeles 39, and 208 Jibboom Street, Sacramento), and treating vermiculite from Libby, Montana; and the other operated by the La Habra Stucco Company (1631 Lincoln Avenue, Anaheim) and treating vermiculite imported from South Africa.

*Utilization.* The most useful properties of muscovite are perfect cleavage, high dielectric strength, low conductivity of heat and electricity, heat resistance, flexibility, transparency, nonflammability, chemical inertness, sheen, and good lubricating qualities. The first listed properties are generally the more important in the uses of sheet mica, whereas the last listed are particularly significant in the uses of serap and flake mica. Indeed, the uses of sheet mica and serap and flake mica differ so greatly that these materials are, in effect, two separate mineral commodities.

In 1955, about 2.4 million pounds of the 4 million pounds of muscovite block and film mica that was cut or stamped by fabricators in the United States, was consumed as insulating material in electronic equipment (U. S. Bur. Mines Mineral Industry Surveys, MMS No. 2498). Nearly nine-tenths of the 2.4 million pounds was used in radio and television tubes and about one-tenth in capacitors and other electronic items. As phlogopite has a higher power factor than muscovite, it is not used in capacitors or other electronic devices that require low power loss. The remaining 1.6 million pounds, which consisted largely of lower quality sheet muscovite, was used mostly as insulation in flotoations, toasters, and other household appliances. An additional 6.4 million pounds, in the form of splittings, was used making built-up mica (alternate layers of binder and irregularly arranged splittings). Built-up mica insulators are essential parts of electric motors, generators, and transformers.

Although sheet mica and built-up mica are used abundantly in electrical equipment that is made and/or sold in California, no mica fabricating plants exist in the state. Such mica is fabricated in plants east of the Missis-



issippi River and close to the major production centers for electrical equipment.

Dry-ground mica is employed mostly as a coating for prepared roofing surfaces. This is by far the principal use for the flake mica mined in California. Dry-ground mica also is used as a filler in roofing, and rubber, as a constituent of wall-board joint cements, paint, plastics, well-drilling muds, welding rod coatings, axle greases and oil, as Christmas tree snow, as thermal insulation, and for numerous other applications. Wet-ground mica, including that brought into California, is used largely as a paint extender and as a filler in rubber.

As expanded vermiculite has a very low apparent specific gravity, relatively high refractivity, low thermal conductivity, and chemical inertness, it is most used as a thermal and acoustical insulating material. As loose fill, it is placed in the open spaces in walls, roofs, and ceilings, on the roofs of furnaces and kilns and in a wide variety of appliances. Chemically treated expanded vermiculite is used as aggregate in light-weight concrete and plasters. All but a very small part of the expanded vermiculite marketed in California is used for insulation or aggregate. Other uses for expanded vermiculite include the following: a constituent of various bonded and molded articles used primarily for insulation; a constituent of roofing and flooring compositions; a soil additive; and as a soil conditioner. In all of its uses, vermiculite is competitive with one or more other materials, principally diatomite, expanded perlite, pumice, volcanic cinders, mineral wool and fiber glass.

*Prices and Marketing.* In 1956 the prices paid by fabricators for the various grades of sheet mica ranged from several cents a pound for punch mica to \$8 or more per pound of clear muscovite in 8 in. x 10 in. sheets or larger (Eng. and Min. Jour. Metal and Mineral Markets). The General Services Administration's price schedule, established in 1952 for purchases of domestic mica for the national stock-pile, ranges from \$1.60 per pound for heavily stained half-trimmed circle and punch to \$70 per pound for clear, full-trimmed clear muscovite in sheets about 3 inches on a side or larger. The G. S. A. also will purchase specified hand-cobbed mica for \$600 per ton.

The 1956 prices in North Carolina for wet-ground mica ranged from \$140 to \$155 per ton, depending on fineness and quality. Dry-ground mica ranged in price from \$32.50 to \$70 per ton. In California the prices were several dollars per ton higher and unground, high-quality scrap mica was valued at about \$45 per ton. Ground mica brought into California from the operation in Petaca, New Mexico, was selling in the Los Angeles area within the general range of \$75 to \$120 per ton. In 1956, the sericite mica which is quarried at the Pacific pyrophyllite mine was being sold in the Los Angeles area for about \$40 per ton; whereas the Los Angeles price for Marter-White was about \$22.50 per ton and ground flake mica was valued at about \$10 per ton. In 1956, the value of crude vermiculite delivered in California was estimated to lie within the range of \$20 to \$30 per ton, depending upon quality.

As all of the domestic mica fabricators are in the eastern United States, no market for sheet mica has been

established in California. Should a commercial source of sheet mica be discovered in the state—an event deemed unlikely by many members of the mica industry—the operator could ship film mica to fabricators, or could ship block or film mica to the government stockpile for the duration of the mica purchasing program. Shipments to the mica stockpile, whose nearest depot is at Custer, South Dakota, must be in minimum lots of 45 pounds for film mica or 1000 pounds for hand-cobbed mica.

The only firm in California known by the writer to be currently (1956) purchasing scrap mica, is the previously noted Sunshine Mica Company of Los Angeles. Although this concern has purchased no scrap mica from local deposits, it constitutes a potential market for material of plus 95 percent purity. Although no vermiculite has been produced commercially in California, local sources are sought by the vermiculite-expanding companies. None of the California concerns that deal in mica products purchases unground mica schist. The ground scrap mica that is brought into California is handled by jobbers in the Los Angeles and San Francisco areas. The total market in California for all grades of ground mica probably lies within the range of 8,000 to 12,000 tons per year.

*Synthetic Mica.* As sheet mica continues to be a strategic material in short supply, in recent years much research has been directed toward the production of synthetic mica. Several methods that are commercially feasible or nearly so have been developed (Dietrich and Thomson, 1956, pp. 17-18), but the production of crystals larger than 2 inches in diameter had not been accomplished by 1955. The synthetic mica was being used to form "reconstituted sheets" for non-strategic uses.

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## MINOR METALS

By J. GRANT GOODWIN

"Minor metals" is a term that is loosely applied to a group of metals each of which is uncommon and used in much smaller amounts than the common base metals. Of the eight minor metals described herein, six are recovered from residues collected in the smelting and refining of sulfide ores. Gallium, germanium, indium, and thallium are recovered from zinc residues; selenium is recovered from copper residues, and rhenium is recovered from molybdenum residues. Cesium and rubidium are recovered from pegmatite minerals.

Most of these metals probably have been obtained from ores mined in California, but no data are available on their distribution or recovery by the custom smelters. Flue dusts and other residues from American Smelting and Refining Company's smelter at Selby, California, as well as from other western smelters, are treated at the Globe smelter in Denver where the minor metals are recovered and refined.

Although the quoted prices of the minor metals in the refined state range from a few dollars to several hundred dollars a pound, these prices partly reflect the cost of refining, and the producers of the ores commonly receive no payment for the contained minor metals.

Many persons who are unaware of this practice and who note that rare metals appear in spectrographic analyses of mineral or rock specimens, are apt to overestimate the value of the material.

*Cesium and Rubidium.* Cesium and rubidium are similar in occurrence, properties, and uses. Both are soft, silver-white metals, liquid at near room temperature. Both are alkali metals. Cesium has a specific gravity of 1.87 and rubidium has a specific gravity of 1.532. Both metals react with oxygen and water and, therefore, must be stored in a vacuum or in an inert liquid.

The principal occurrence of cesium and rubidium is in the mineral pollucite (hydrous cesium-aluminum silicate) which occurs only as a rare constituent of pegmatites. Cesium and rubidium are also found in lepidolite (lithia mica) which also occurs in pegmatites. The mineral pollucite is the principal source of cesium and rubidium; it contains as much as 36 percent cesium oxide and about 3 percent rubidium oxide. Cesium and rubidium also are minor constituents of some beryl, carnallite, and rhodizite. Pollucite has been reported in the pegmatites of San Diego County, but these occurrences have not been of commercial importance.

Cesium and rubidium because of their sensitivity to light have been employed in photography, television, signaling devices, scintillation counters, optical detection devices, vapor lamps for infrared signaling, and in infrared photography.

At present the cesium and rubidium supply is adequate to meet the demand. The principal sources are pegmatites in Africa, Brazil, South Dakota, and Maine. Pollucite ore containing about 25 percent cesium oxide has been sold at \$400 to \$600 per ton in recent years, as compared to \$30,000 per ton in 1927 (Sargent, 1956). Cesium metal is quoted at \$2.00 to \$5.00 per gram (Sargent, 1956).

*Gallium.* Gallium is a gray metal which is liquid at or near room temperatures. The liquid has greater density than the solid and has low vapor pressures even at elevated temperatures. Gallium remains a liquid over a very wide temperature range (85.5° F. to 3,601° F.). It has a specific gravity of 5.9, it is brittle, and has a hardness of 1.5 to 2.5 (Mohs' scale).

Gallium is as plentiful as lead in the earth's crust, but is much more widely dispersed. Because of its chemical similarity to aluminum, gallium is concentrated in clay-rich soils and clay minerals, particularly in bauxite. It is also concentrated by some plants and, therefore, exists in certain coal deposits. Germanite, a complex zinc-copper-arsenic-germanium sulfide which is locally associated with lead-copper ores contains from 0.1 to 0.8 percent gallium (Thompson, 1954). Although germanite contains the highest known percentage of gallium of any mineral, its rarity excludes it as a possible commercial source of gallium. Zinc ores of the Tri-State (Missouri-Oklahoma-Kansas) district are known to contain from 0.001 to 0.02 percent gallium (Thompson, 1954). The gallium content of zinc ores from California is not known to the writer nor has the gallium content of California coals and clays been investigated.

The uses of gallium are limited mainly because of its scarcity, high cost of extraction and purification, and its corrosive nature. The wide temperature range through which gallium remains a liquid makes it of use in high temperature thermometers and in special use alloys. Gallium surfaces will reflect a high percentage of incident light and for this reason gallium may find use in special mirrors. The Atomic Energy Commission has investigated gallium as a heat transfer medium, but corrosion problems are great. The use of radioactive gallium in the detection of bone cancer also is being investigated (Dudley, 1949). Uses would probably increase if a larger and cheaper supply were available.

Gallium is obtained commercially by the treatment of residues from aluminum and zinc smelting and refining. Several chemical leaching and purifying processes are used in the recovery of gallium. The principal producers of gallium in the United States are Eagle-Picher Company and Aluminum Company of America. In 1948, the domestic production of gallium was about 200 pounds and during the same year sales were estimated at 100 pounds (Thompson, 1954). In recent years, the demand has been very small and production has not been reported. The quoted price (American Metal Market, May 29, 1956) is \$1,362 per pound. This is less than one-tenth of the quoted price in 1930. In 1956 supply was more than adequate to meet the demand. Twenty tons of gallium per year probably could be produced in the United States if the demand existed (Atomic Energy Commission, 1950).

*Germanium.* Germanium is a brittle gray-white metal with a hardness of 6.25 (Mohs' scale), a specific gravity of 5.32, a melting point of 958.5° C. and a boiling point of approximately 2700° C.

Germanium occurs as a minor constituent in the sulfides of zinc, copper, and silver, and in trace amounts



in coal deposits. Argyrodite (silver-germanium sulfide) contains from 5 to 7 percent germanium. Canfieldite (silver-tin-germanium sulfide) ideally contains 1.8 percent germanium. Germanite (copper-zinc-arsenic-germanium sulfide) contains as much as 10 percent germanium. Renierite (copper-iron-germanium arsenic sulfide) averages about 7 percent germanium. Enargite (copper arsenic sulfide) from the western United States has a maximum germanium content of about 0.03 percent (Harner, 1954). These minerals are rare, however, and none has been an important source of germanium. Virtually all the germanium produced in the United States is recovered by the Eagle-Pitcher Company during the treatment of zinc ores from the Tri-State district. These ores yield sphalerite (zinc sulfide) concentrates which contain 60 percent zinc, and from 0.01 to 0.015 percent germanium. The germanium is extracted from dust collected in electrostatic precipitators at the zinc smelter, and is chemically leached and purified by a complex process. Germanite- and renierite-bearing copper ore from Africa may become the world's leading source of germanium within the next few years (Eng. and Min. Jour., May 1956).

Germanium, a metalloid, is of value principally because it is a semi-conductor. This property has made germanium of great value in the electronic industry, where it was first used as a diode crystal rectifier, and later in the germanium triode or transistor. The transistor largely replaced the larger, more fragile, and less efficient vacuum tube in many of its applications. Another possible use of germanium is in germanium-gold alloys for dental purposes; the alloy expands upon solidification.

The nonmilitary consumption of germanium by the electronic industry has risen from 12,000 pounds in 1953 to an estimated 39,000 pounds in 1955 (Sargent, 1956). An estimated 100 tons of germanium is contained in the reserves of lead-zinc ore in the Tri-State district (Sargent, 1956).

The present price of germanium is \$44.50 to \$53.50 per gram (Am. Metal Market, May 29, 1956). This is less than one-fifteenth of the price paid for germanium in 1940. The present demand is strong and will grow with the electronic industry. High-purity silicon will compete in some fields, but is expensive to produce.

**Indium.** Indium is a soft gray metal resembling tin. It is softer than lead and is extremely plastic. It can be deformed almost indefinitely without becoming work hardened. It is stable in air and corrosion resistant. Indium has a melting point of 155° C., a boiling point of 1450° C., and a specific gravity of 7.36. Indium has a viscosity that changes very slightly over a wide temperature range. The metal has important lubricating properties, and alloys readily with other metals.

Indium is not an essential constituent of any of the known minerals, but is widely dispersed in the earth's crust. It is found in proportions of as much as one percent in iron-rich sphalerite, in tin ores, and in tungsten ores. It also occurs in pegmatites and has been reported in alunite, manganotantalite, phlogopite, pyrrhotite, rhodonite, samarskite, and siderite.

Because of its mechanical and chemical properties, indium has a wide variety of uses and a great potential

for new uses. The principal use for indium is in sleeve bearings for aircraft engines. In addition to its lubricating properties, indium hardens lead, thus making a more durable bearing. Indium also resists the acids in lubricating oils. Because of the low melting point of indium alloys, indium is used in a variety of special alloys. Certain indium alloys such as tin-indium alloy are capable of wetting glass and therefore find use as glass-to-glass or glass-to-metal seals. Indium is also used in special solders, dental alloys, with germanium in junction-type transistors, as a color reflecting medium, as a pigment in glass, and in the chemical industry. Research is being conducted on the possible uses of indium compounds in the electronic field. The oxides, selenides, and tellurides of indium are semi-conductors. Possible future applications for indium compounds include: (1) the addition of indium to chromium plating baths to reduce brittleness of the chromium plate; (2) the use of indium in magnetic alloys; (3) the use of indium compounds as photoconductors in electro-photographic plates; (4) indium sulfide phosphors; (5) use of indium compounds (which are semi-conductors) as rectifiers; (6) the use of indium oxide as a resistor; (7) the use of indium in small quantities as a stabilizer in semi-conductors; (8) the use of indium in indium-titanium alloys to increase strength and decrease ductility; (9) use of indium in low-resistance contacts in electrical circuits; (10) the use of indium as an indicator in the atomic pile because of the ease with which indium is made artificially radioactive by neutrons of low energy; and (11) the possible use of indium trisulfide as a thermistor because of its large negative coefficient of resistivity and its chemical and electrical stability at high temperatures.

Most of the commercial production of indium is obtained from the chemical treatment of flue dust and other residues at lead and zinc smelters. The current annual production in the United States is about 10 tons and it is estimated that another 90 tons per year is probably lost in residues not treated for indium (Sargent, 1956). During the period 1942-54 the price of indium dropped from \$30.00 to \$2.25 per troy ounce. The present quoted price is \$2.25 per troy ounce (Am. Metal Market, May 29, 1956). The supply is sufficient to meet the demand at this price, but the demand is expected to increase.

**Rhenium.** Rhenium is a silver-white metal with a specific gravity of 20.53. It has a melting point of 3440° C. and a boiling point of about 5900° C. Rhenium alloys with tungsten, nickel, cobalt, tantalum, platinum, rhodium, iridium, gold and iron.

Although no minerals are known that contain rhenium as an essential element, it is widely dispersed in the earth's crust. It is concentrated in molybdenite in proportions of as much as 0.30 percent (Sargent, 1956). Rhenium is also reported to occur in gadolinite (a beryllium-rare earth silicate), other rare earth minerals, columbite, tantalite, platinum ores, copper sulfides, and manganese oxides.

Rhenium has found limited use in industry, principally because of its scarcity and high cost. High-temperature rhenium-bearing alloys with high corrosion-resistant properties have been investigated. Rhenium



may also be used with rhodium, iridium, and platinum in thermocouples which have high electromotive forces. Rhenium filaments may find use in electronics. A number of British and American patents have been issued for special-use rhenium alloys and catalysts.

Rhenium is commercially extracted from flue dust residue collected in the roasting of molybdenite concentrates from Arizona. The rhenium-bearing molybdenite occurs in copper ore mined near Miami, Arizona. Over a 10-year period, 17 tons of molybdenite roaster flue dust have been chemically processed at the University of Tennessee. About 240 pounds of rhenium in the form of potassium perrhenate have been extracted (Melaven, 1954). Rhenium metal is quoted at \$900 per pound (Sargent, 1956).

**Selenium.** Selenium is a gray crystalline solid with a semimetallic luster. It is a semimetal found with and related to sulfur and tellurium. It has a specific gravity of 4.81, a melting point of 217° C. and a boiling point of 688° C. Its physical and chemical properties are similar to those of sulfur.

Selenium is found in native sulfur and occurs in the form of selenides of lead, silver, copper, and zinc. Selenium is present in many base metal ores in proportions of as much as 0.02 percent (Sargent, 1956).

Selenium has a wide variety of commercial uses which would be even more numerous if sufficient supplies were available. The oldest and one of the largest uses for selenium is in the glass and ceramic industries. When added to glass in small amounts, selenium acts as a decolorizer. Cadmium-selenium lithopones are used for making non-fading red paints, and cadmium-selenium reds are used in making ruby-red glass and glazes. Perhaps the most important use of selenium at the present time is in the electronic industry where selenium, owing to its semiconductivity, is of great value as a rectifying medium. This use for selenium is growing rapidly. The U. S. Signal Corps is using selenium in aerial photography in a new printing process called xerography. Selenium added to steel or copper greatly increases the machinability of the metals. Other uses for selenium include: (1) an additive in rubber; (2) an antioxidant additive to lubricating oils; (3) selenium dioxide as an oxidizing agent in the preparation of cortisone; (4) flame-proof and corrosion-resistant coatings of fabricated products; (5) insecticides; (6) use in photography in photoelectric cells; (7) in the oxychloride form as a powerful solvent; and (8) a wide variety of industrial chemicals.

Most of the commercial output of selenium is obtained from slimes which are a residue in the electrolytic refining of copper. Blister copper contains about 0.05 percent selenium (Sargent, 1956). In the United States it is produced by American Smelting and Refining Company, Anaconda Company, and Kennecott Copper Corporation. The selenium is derived principally from the copper ores of Utah, Arizona, New Mexico, and the states of Durango and Zacatecas in Mexico. From 1945 to 1955, domestic production rose from about 500,000 pounds per year to 700,000 pounds per year. In 1956 the annual rate of consumption in the United States was about 1,000,000 pounds and the demand was about 1,500,000 pounds per year. The price rose from \$1.75 per pound in 1947 to

\$15 to \$20 per pound in 1956. Commercial grade selenium is 97.2 to 99.94 percent pure.

Some selenium is currently being recovered by Anaconda Company from the processing of sulfur mined at the Leviathan sulfur mine in Alpine County, California. No other data are available on selenium recovered from California ores.

**Thallium.** Thallium is a soft bluish-white metal with a specific gravity of 11.85, a melting point of 302° C., and a boiling point of 1457° C. It alloys readily with most other metals but not with copper, aluminum, manganese, nickel, zinc, and selenium.

Thallium occurs in minute quantities in the sulfides of the common metals. Three thallium minerals are known, but they have not been found in commercial quantities. They are: vrbaite (sulfide of thallium, arsenic, and antimony), lorandite (sulfide of thallium and arsenic), and hutchesonite (sulfide of lead, thallium, silver, and arsenic). Thallium also occurs in certain potash minerals (Howe, 1954).

The principal use for thallium is in insect and rodent poisons. In these, thallium sulfate, a tasteless and odorless but very toxic chemical, is used. The photosensitivity of thallium salts make them of value in scintillation counters, infrared signaling and detection devices, as a phosphor activator, and in various optical instruments and lenses. Thallium is of value as a catalyst in the reduction of nitrobenzene by hydrogen, and has some medicinal uses. A few special-use alloys have also been developed. The most promising is a thallium-mercury alloy that will not freeze in the arctic and antarctic regions and in the stratosphere. The alloy may therefore be substituted for mercury in switches and seals which must operate at temperatures as low as -76° F.

Commercial thallium is produced in the United States principally by American Smelting and Refining Company. It is obtained from flue dusts and other residues that are recovered as by-products of the roasting of pyrite for sulfuric acid and of the roasting of lead and zinc ores. The extraction of the thallium from these residues is dependent largely upon the ease of solubility of thallium in a weak acid. The supply of thallium is sufficient to meet present demand and an increase in demand caused by new uses could easily be met. In 1956 the quoted price for thallium was \$12.50 per pound (Am. Metal Market, May 29, 1956).

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## MOLYBDENUM

By RICHARD M. STEWART

Numerous occurrences of molybdenum minerals exist in California, and molybdenum ore has been produced intermittently in the state since 1916. Most of the total output has been a by-product of the Pine Creek tungsten operation in Inyo County (see section on tungsten), and has reflected the activity at this tungsten mine. The most productive period in California was 1941-43 when about 3½ million pounds were produced. During this period California ranked among the first six molybdenum-producing states. Annual production figures for most years are not available, but during 1952, when California ranked fifth as a molybdenum source, the Pine Creek tungsten mine yielded about 300,000 pounds of molybdenum (H. L. McKinley, 1953, personal communication). During 1952, 43,259,000 pounds of molybdenum were produced in the United States.

Of all the alloying elements utilized in steel manufacture, molybdenum is the only one in which the United States is self-sufficient. This country's molybdenum resources constitute a larger percentage of known world molybdenum resources than that of any other metal in common use (U. S. Bureau of Mines, 1948, p. 144).

*Mineralogy and Geology.* Molybdenum does not occur free in nature; almost all of the world's molybdenum is obtained from the primary mineral molybdenite ( $\text{MoS}_2$ ). Molybdenite is a soft (hardness 1 to 1½), bluish lead-gray mineral with a bluish to greenish-gray streak and a metallic luster. It crystallizes in the hexagonal system, and most commonly occurs as flakes and foliated masses. It can be distinguished from graphite, which it strongly resembles, by the violet color shown in a cleavage crack and by its lighter bluish lead-gray color. Wulfenite ( $\text{PbMoO}_4$ ), a minor source of molybdenum, is relatively common in the oxidized zone of some galena- and molybdenite-bearing deposits. Powellite ( $\text{Ca}(\text{Mo},\text{W})\text{O}_4$ ), an oxidation product of molybdenite, commonly is of little commercial importance, but both tungsten and molybdenum are recovered from it at the Pine Creek mill.

Molybdenite has a wide range of geologic occurrences, but nearly all are genetically related to acidic igneous rocks. Commercial quantities of molybdenite have been recovered from fissure veins, disseminated replacement deposits, contact-metamorphic deposits, and pegmatites. In the world's largest molybdenum deposit at Climax, Colorado, molybdenite occurs with quartz and orthoclase in veinlets within altered portions of a granite mass. Although material containing 0.7 percent  $\text{MoS}_2$  was regarded as ore in the early 1930s and the average grade of ore milled had been 0.83 percent  $\text{MoS}_2$  (Butler, 1933, p. 231), ore that contains only 5 to 6 pounds of molybdenum (equivalent to 0.5 percent  $\text{MoS}_2$ ) is now being milled (Climax, 1954, p. 5). A mine at Questa, New Mexico, yields molybdenite from quartz veins in granite. Ore from this deposit averages about 5 percent molybdenite (Tyler, 1952, p. 84), an unusually high grade. Disseminated copper deposits of the western United States contain minor amounts of molybdenite. The copper deposits at Bingham, Utah, where molyb-

denite is recovered as a by-product, have become the world's second largest molybdenum source. The  $\text{MoS}_2$  content here ranges from 0.04 to 0.20 percent.

Contact-metamorphic deposits, such as those that are worked for tungsten at Pine Creek in California, commonly contain recoverable amounts of molybdenite. Though molybdenite is an accessory mineral in some granites, pegmatites and aplites, it rarely occurs as commercial concentrations in these rocks. Nevertheless, a small portion of the molybdenite mined in California has been obtained from aplite dikes, principally in San Diego County.

Some clays and other sedimentary rocks, including the vanadium-bearing phosphatic shales of Idaho, Wyoming and Montana, contain molybdenum in proportions ranging from a few hundredths to 0.1 percent (Tyler, 1952, p. 84). Molybdenum possibly could be recovered as a by-product if these materials were processed to recover vanadium.

*Localities.* At the Pine Creek mine in Inyo County, the tungsten-molybdenum ore bodies occur in a contact zone near the north end and on the west side of an elongate mass of metamorphic rocks surrounded by intrusive granite and quartz diorite. The contact zone consists of tectite, quartz, and quartz-feldspar rocks. The deposit and mine workings are described in the tungsten section of this bulletin. Molybdenite and powellite are present in all of the five known ore bodies. In two of these, molybdenite occurs in well-defined ore shoots which are more closely associated with the quartzose parts of the contact zone than with the tectite. Some ore, although containing scheelite, was mined primarily for its molybdenite content (Bateman, 1945, p. 238).

The molybdenum content of the ore mined has decreased with depth. The average grade of ore mined from the upper workings in the 1940s ranged from 0.40 to 0.45 percent  $\text{MoS}_2$  (Bateman, 1945, p. 238. Norman, 1951, p. 93); this is equivalent to 0.24 to 0.27 percent Mo. Ore mined from the Zero-level workings in 1952 contained 0.12 percent Mo (H. L. McKinley, 1953, personal communication) and in 1953 and 1954 contained 0.096 and 0.097 percent Mo respectively (H. L. McKinley, 1955, personal communication).

Aplite dikes in San Diego and Shasta Counties contain molybdenite in small thin flakes scattered throughout. Large concentrations of economic grade are not known. Visual estimates of the grade of molybdenum deposits in aplite dikes are apt to be too high because molybdenite's thin flaky habit makes it appear more abundant than it is. Several dikes in the vicinity of Ramona and Campo, San Diego County, have been explored, however, and small amounts of molybdenite concentrates produced (Tucker, 1939, pp. 30-31). On the Bour deposit near Ramona, a dike 30 feet wide was explored by an open cut about 110 feet along its strike; two zones, 10 and 50 feet long, contained a higher than average concentration of molybdenite, but even these proved to be of sub-commercial grade. Small production



has been reported from a similar deposit near Gibson in Shasta County (Averill, 1939, pp. 168-169). None of these deposits has been active in recent years.

Small amounts of molybdenite also have been produced as a by-product from a copper deposit in Plumas County (MacBoylé, 1920, p. 180), and from a molybdenite-bearing quartz vein in San Bernardino County (Wright, 1953, pp. 121, t. 93).

**Utilization.** The demands made upon modern industrial technology to produce new machines and equipment capable of greater efficiency and versatility and higher speeds have in turn increased the requirements for metals of greater strength and hardness and possessing greater resistance to high temperatures, corrosion, and abrasion. Molybdenum, as an alloying element or as pure metal, contributes substantially to our ability to meet these requirements. These metallurgical uses account for nearly 95 percent of the domestic molybdenum consumption.

Pure molybdenum melts at 2625° C (4757° F), a melting point nearly two and a half times that of copper, about twice that of steel, and exceeded by only four other elements: carbon, rhenium, tantalum, and tungsten. Molybdenum is heavier than copper or iron, having a density of 10.2 grams per cubic centimeter. Compared with similar properties of copper, molybdenum's thermal conductivity is less than a half, its electrical conductivity about one-third, and at room temperature its coefficient of expansion is about 30 percent.

*Distribution of molybdenum by uses for 1952, derived from reports of the National Production Authority (Geehan, 1954, p. 4).*

Metallurgical -----	Total: 94.8 percent
Steel -----	63.7
Gray iron and malleable castings -----	27.8
Molybdenum metal -----	1.9
Welding electrodes -----	1.4
All other -----	Total: 5.2 percent
Paint and pigments -----	1.8
Catalysts -----	0.8
Lubricants -----	0.3
Miscellaneous (includes chemicals and non-ferrous alloys) -----	2.3

Molybdenum is one of the most versatile alloying metals in the production of high quality steel. It has no deoxidizing or scavenging properties, and is used strictly as an alloying element. Large amounts of molybdenum are substituted for tungsten to provide hardness at red heat, commonly known as "red-hardness," in high-speed steels used for all types of cutting tools. Almost all nitriding or case-hardening steels contain molybdenum, which adds to their strength. The addition of molybdenum to stainless steels increases their resistance to chemical corrosion. Molybdenum is one of the best additives for providing high-temperature strength to steel alloys, such as those used in jet-propulsion engines, and is one of the few alloying elements that does not adversely affect the weldability of the steel. Molybdenum is also commonly used to improve the strength and toughness of cast iron. The continuing large scale development and exploitation of the deposit at Climax, Colorado, has been possible only because of the many metallurgical uses.

Pure molybdenum is a soft, ductile, white metal possessing a high melting point and thermal conductivity. In recent years, considerable interest has been shown in the pure metal because of these qualities, and molybdenum has many uses in the form of finished rod, wire, or sheet. Molybdenum wire, 0.003 to 0.050 of an inch in diameter, is used for filament supports in incandescent lights, and grid elements in radio tubes. It is used extensively in the form of ribbon, 0.006 to 0.010 of an inch thick, for heating elements in electric-resistance furnaces. Temperatures up to 2000° C (3632° F) can be obtained. Molybdenum electrical contact points give excellent results.

Molybdenite added to oil or grease provides these lubricants with special qualities, such as ability to resist high pressures and to give adequate lubrication under extremely low temperatures. Molybdenum as sodium molybdate is important as a trace element additive to soil; thousands of acres of once-barren land in Australia were rehabilitated by this use. Molybdenum is also used in the preparation of inks and fast dyes; with nickel it serves as a catalytic agent in the hydrogenation of oils; lead molybdate is an opacifying agent in the production of glass enamels.

**Mining Methods and Treatment.** Most of the ore at the Pine Creek tungsten mine is produced from sub-level stopes that progress by blast-holes ringed out from sub-level drifts; some smaller shrinkage stopes are active. In contrast to this operation is the large-scale block caving system employed at Climax, Colorado. During 1954, expansion there was completed to allow the mining of about 28,000 tons of ore per day. Most of the copper properties that also yield molybdenite are mined by large-scale open-pit methods.

The milling and concentration of molybdenum ore is fairly simple inasmuch as molybdenite is one of the minerals most amenable to the flotation process. Flotation is the standard concentration process for molybdenite. The chief problem in the flotation of molybdenite is depressing copper sulfides, but reagents have been developed to successfully meet this problem.

For use in the steel industry, molybdenite concentrate normally must be converted to either molybdenic oxide, calcium molybdate, or ferromolybdenum. The molybdenite concentrate is first roasted to technical grade molybdenic oxide at temperature controlled to prevent high volatilization loss. This technical grade oxide is the raw product from which the other molybdenum-bearing materials are converted. Volatilization of the technical grade oxide in an electric furnace at approximately 1800° F will form pure molybdenic-oxide powder.

Calcium molybdate can be made in either of two ways. Lime can be added to the technical grade molybdenic oxide while it is still in the roasting furnace and after the sulfur has been virtually eliminated from the molybdenite, or more commonly, uncalcined high-quality limestone can be mechanically mixed with the roasted concentrate. This "calcium molybdate" normally contains 46.3 percent Mo (Hayward, 1952, p. 519).

Ferromolybdenum is usually made by the thermite process. This process, as employed at the Langeloth, Pennsylvania, plant of the Climax Molybdenum Company (Wheeler, 1944, p. 439), requires a mix of 1300



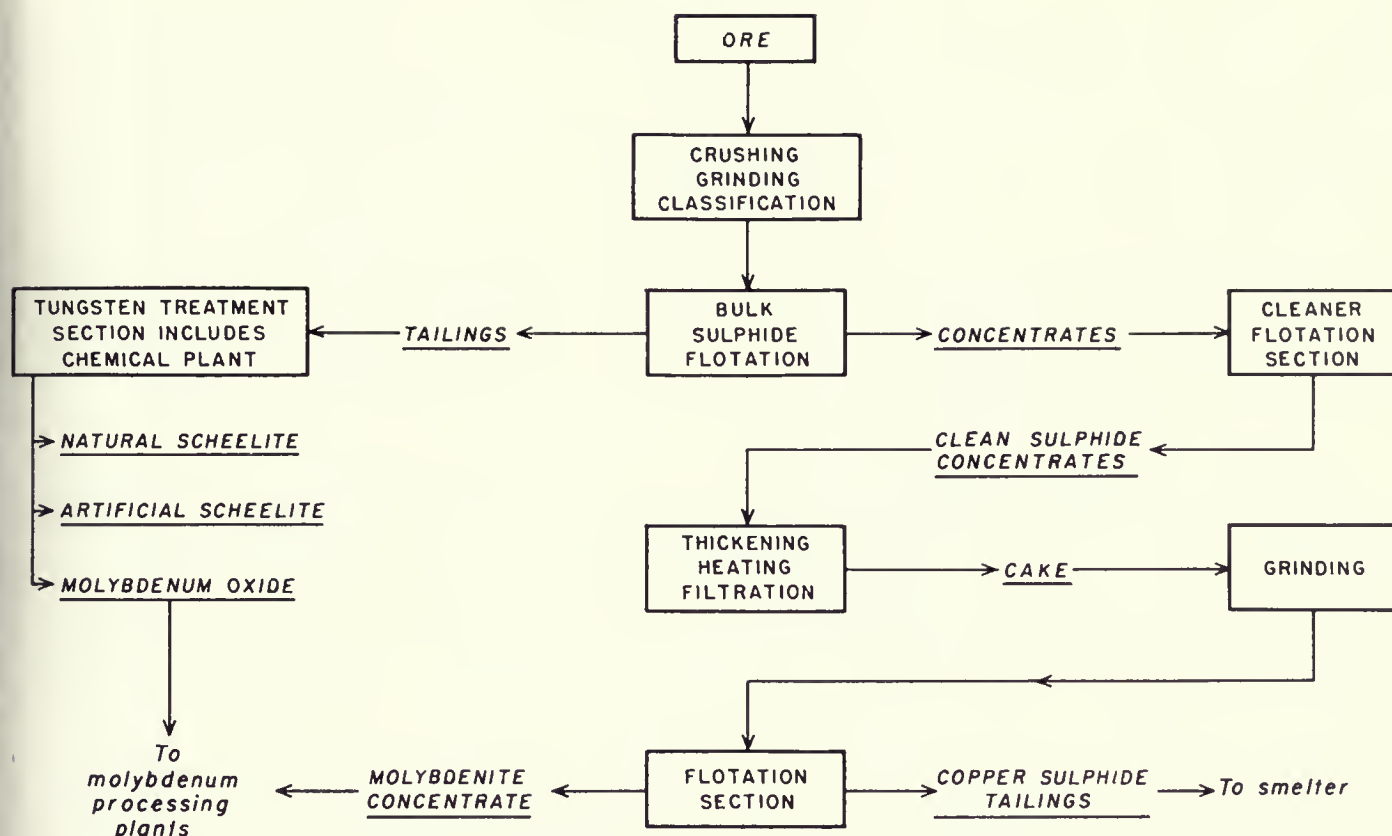


FIGURE 1. Summary of molybdenum section, Pine Creek tungsten mill (from text by Behme, 1953, pp. 58-59).

pounds of molybdenum contained in oxide, 116 pounds of impure aluminum (93 percent aluminum), 1122 pounds of ferrosilicon (50 percent silicon), 618 pounds of iron ore (69 percent iron), 160 pounds of lime, and 50 pounds of fluorspar (95 percent  $\text{CaF}_2$ ). The mix is dumped into a reaction pot, a bottomless brick-lined steel shell set over a shallow pit scooped in wet sand, and the reaction is started by igniting the charge with a fuse of aluminum and sodium peroxide. The reaction is complete in 15 to 20 minutes and yields a slag-covered button of ferromolybdenum weighing around 2000 pounds. It is cleaned of slag, after cooling and quenching in water, and crushed to market size. The thermite process is also used to make molybdenum silicide, a less commonly used alloying material.

Molybdenum metal is made by dissolving the oxide in ammonia and precipitating ammonium molybdate. Application of heat to this produces molybdenum trioxide which in turn is reduced to pure molybdenum by heating in a current of hydrogen at  $900^\circ\text{C}$  to  $1000^\circ\text{C}$  (Hayward, 1952, p. 520). The product, a grayish-black powdered metal, is pressed into 12-inch bars, a quarter to half an inch thick, and heated between contacts in hydrogen to a temperature slightly below the melting point. The resulting porous bar can be hot-worked to fine wire, sheet, or rod.

Many uses of molybdenum require it in the form of large sheets or sections from which impurities, especially oxygen, have been virtually eliminated. To meet these needs, new techniques have been developed in which large ingots are produced in vacuum furnaces (Geehan, 1954, p. 8).

The two principal molybdenum companies, Climax Molybdenum Company and Molybdenum Corporation of America, convert their concentrates to finished end products at plants in Langeloth, Pennsylvania, and Washington, Pennsylvania, respectively.

**Markets.** With the start of the Korean war in 1951, molybdenum as well as other alloying elements, was in short supply throughout the free world.

Table 1. Buyers and specifications for molybdenite concentrates.

Specifications	General Services Administration government stockpile (analysis on a dry basis)	Molybdenum Corp. of America, 406 S. Main St., Los Angeles 13, California	Climax Molybdenum Co., 500 5th Ave., New York 36, New York
MoS <sub>2</sub> —minimum %	80.00	90.00	86.00
Cu—maximum %	1.00	0.50	0.50
Pb—maximum %	0.30		0.10
P + As + Sn — maximum %	0.20		
Moisture (H <sub>2</sub> O) maximum %		1.00	4.00
Flotation reagents (oil, etc.) maximum %			5.00
Price	Subject to negotiation but generally based upon E. & M. J. Metal and Mineral Market quotation.*		\$1.00 per lb., f.o.b. Climax, Colorado, (late 1954).

\* A price of \$0.60 per pound of contained MoS<sub>2</sub> was quoted in the Engineering and Mining Journal Metal and Mineral Markets during the interval 1950 through 1954. Inasmuch as molybdenite, MoS<sub>2</sub>, contains 60 percent Mo, that price is equivalent to \$1.00 per pound of contained Mo. The price quoted in 1955, through November, was \$1.05 per pound of contained Mo, f.o.b. Climax, Colorado, plus cost of containers.



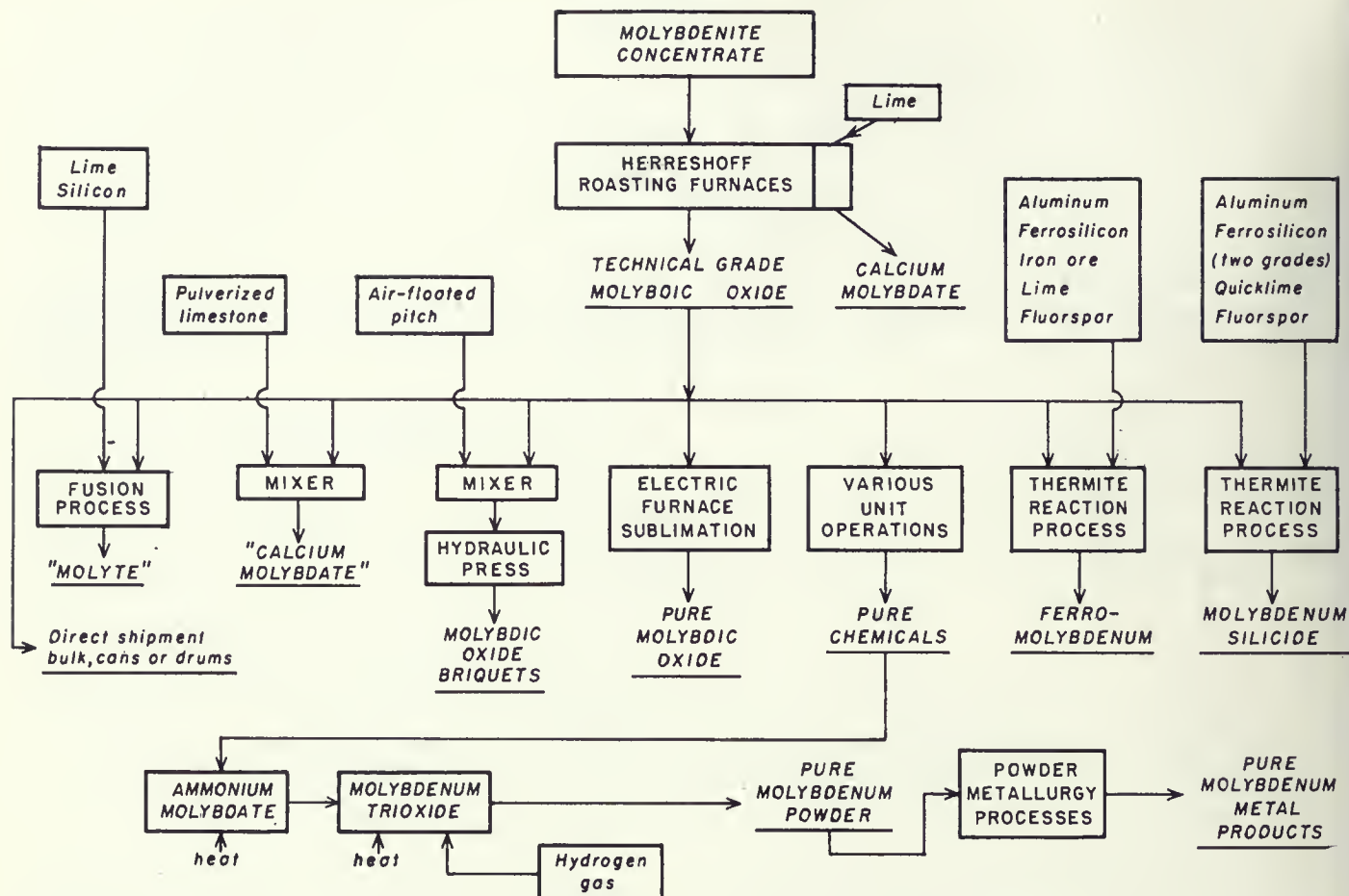


FIGURE 2. Summary flowsheet of molybdenum processes (adapted from Wheeler, 1944, pp. 433, 435, and Hayward, 1952, pp. 515-520).

Government controls by the National Production Authority, the Defense Minerals Administration (later the Defense Minerals Procurement Agency) and the Office of Price Stabilization included price controls and allocation of molybdenum ore and concentrates and of end products. Controls started in 1951 and continued until July 1, 1953, when allocation was no longer considered necessary.

The program of the Defense Minerals Exploration Administration (DMEA) provides for loans of 50 percent of the cost of approved exploration projects on molybdenum deposits. In addition, the General Service Administration will purchase molybdenum concentrates that meet the stockpile specification (see Table 1).

Inasmuch as molybdenum ore is not marketable as such, a prospective molybdenum producer must be able to provide a concentrate, utilizing his own mill or a custom mill. In 1955, no custom mills were known to have arranged for the processing of molybdenum ore. No attempt to ship concentrates should be made without prior approval from a buyer.

Prices for molybdenum concentrates and finished products did not change in the interval 1950 through 1954, but were slightly increased early in 1955. The finished products were valued f.o.b. producer's plant in November, 1955 as follows:

Molybdenum metal, 99 percent Mo.	-----	\$3.00 per pound	
Ferro molybdenum (58-64 percent Mo)	-----	1.46	Per pound of Mo contained.
Ferro molybdenum (58-64 percent Mo powdered)	-----	1.57	
Calcium molybdate (CaMoO <sub>4</sub> )	-----	1.28	
Molybdic oxide (MoO <sub>3</sub> ) (canned)	-----	1.25	
Molybdic oxide (MoO <sub>3</sub> ) (bagged)	-----	1.24	

*History of Production.* World War I probably was the impetus for the first production of molybdenum in California. The earliest recorded output in the state was in 1916, when a combined total of 8 tons of molybdenum concentrates, valued at \$9,945, was shipped from Inyo and Plumas Counties (Bradley, 1917, pp. 39-40). From 1916 to 1918, small shipments were made variously from Inyo, Mono, San Diego, and Shasta Counties, but in 1918 only Shasta County yielded molybdenum.

Following World War I, the demand for molybdenum was slight, and no ore was mined in California until the period 1933-34 when a small tonnage of ore was shipped from Inyo and Mono Counties.

Production was resumed from Inyo County in 1939 and was continued through 1944. Production in 1943 was the largest of any year (Symons 1944, p. 51). In 1945 the Pine Creek tungsten mill was shut down and there was no molybdenum production. Operations were resumed in 1946 and have continued to date. Although annual production figures are not available for most



years, recent molybdenum production from the Pine Creek operation is tabulated below:

1952	300,000 lbs	(H. L. McKinley, 1953, personal communication)
1953	154,805 lbs	} (H. L. McKinley, 1955, personal communication)
1954	143,211 lbs	

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# NATURAL GAS

By EARL W. HART

The use of natural gas in the United States, and particularly in California, has grown tremendously in recent years. In 1954, natural gas supplied 25 percent of the total energy requirements of the United States, approximately six times the energy supplied by hydroelectric power (Cattell et al., 1955, p. 17). California, fourth in the production of natural gas among the states, contributed about 6 percent of the national total, or about 507 billion cubic feet in 1954. Of the mineral commodities produced in California in 1954, natural gas ranked third in output, having been surpassed only by petroleum and natural-gas liquids. Gas reserves in California have been declining steadily in recent years and any large increase in future reserves will have to result from the discovery of one or more major gas fields or gas-yielding oil fields. The demand for natural gas for heating and fuel purposes will increase in California as new houses are built and industry expands. To meet this demand, additional gas will have to be imported into the state. During 1954, nearly half of the gas used in California was piped in from Texas and New Mexico. Some of the gas used in refineries and in oil field operations is being diverted to industries where a higher market price may be obtained.

**Composition and Geologic Occurrence.** Two types of natural gas, exclusive of carbon dioxide, are of commercial importance in California: (1) dry gas (or marsh gas), the occurrence of which is essentially unrelated to that of petroleum, and (2) wet gas (or oil-well gas, petroleum gas, or casinghead gas), which occurs in the same formations as petroleum and is produced with it. Some wet gas exists as a gas cap above the petroleum and some is dissolved in petroleum in the oil-field reservoir.

The volatile portions of natural gas consist essentially of hydrocarbons of the paraffin (methane) series in which methane ( $\text{CH}_4$ ) is predominant, and in which also occur ethane ( $\text{C}_2\text{H}_6$ ), propane ( $\text{C}_3\text{H}_8$ ), butane ( $\text{C}_4\text{H}_{10}$ ), and heavier paraffin hydrocarbons, listed in order of decreasing abundance. The principal gaseous impurities are nitrogen, carbon dioxide, and hydrogen sulfide. These impurities generally amount to a small percentage of a given natural gas, but may constitute 20 or 30 percent. Wet gas differs principally from dry gas in that wet gas usually contains enough propane, butane, and heavier hydrocarbons to allow for the profitable extraction of natural-gas liquids, whereas dry gas does not. (See section on natural-gas liquids in this volume.) Other differences that generally exist between wet gas and dry gas are: (1) wet gas is lower in methane; (2) wet gas contains a smaller percentage of non-volatile impurities; and (3) dry gas contains much less hydrogen sulfide or none at all. Because the composition of both types of gas varies considerably from one field to another, the heating value is also variable. Such variation in heating value is commonly compensated for by blending gases from several fields, particularly dry gas with wet gas when possible. Wet gas generally has the higher heating value.

Geologic factors necessary for the formation and accumulation of natural gas are similar to those of pe-

troleum, namely: (1) a source rock high in organic matter from which gaseous hydrocarbons may be formed; (2) a reservoir rock to allow for the accumulation of natural gas; and (3) a structural or stratigraphic trap to prevent the loss of the gas by upward migration. The source rocks in California range in age from Upper Jurassic to Pliocene. Dry gas is produced from sandstone reservoirs which underlie the Sacramento and San Joaquin Valleys and which range in age from Cretaceous to Pliocene. Oil-well gas is produced from sandstone and fractured shale that range in age from Cretaceous to Pleistocene and from pre-Cretaceous basement rocks located in the Coast Ranges, San Joaquin Valley, Ventura Basin, and Los Angeles basin. Wet gas has been obtained from virtually every oil field in the state (see section on petroleum in this volume).

Most of the gas produced in California in the past has been wet gas produced along with oil. In 1954, about 75 percent of the net gas withdrawn from formations in California was wet gas.

Table 1. Fields with largest natural gas production in California in 1954.

(Thousands of cubic feet.)

Field	Net gas withdrawn*
<b>Dry gas—gas fields</b>	
Rio Vista.....	67,477,766
Trico.....	7,862,645
River Island.....	4,976,989
Wild Goose.....	4,156,551
McDonald Island.....	3,552,512
<b>Wet gas—oil fields</b>	
Ventura Avenue.....	57,175,330
Kettleman North Dome.....	38,203,470
Wilmington.....	34,018,746
Paloma.....	30,640,803**
Belgian Anticline.....	18,694,246

\* Data from Division of Oil and Gas. Net gas withdrawn includes all gas withdrawn from formations except that which was returned for purposes of repressuring.

\*\* Small amount of gas is from dry gas zone.

**History of Discoveries.** The first useful natural gas produced in California was obtained from the Court House well at Stockton, which was drilled as a water well to a depth of 1,003 feet in 1854-58. Since that time, many other water wells in the Stockton area have encountered gas which was used locally for lighting and heating purposes (Weber, 1888, pp. 181-85). In 1891, gas was discovered in water wells near Sacramento and has also been used. A gas well drilled at Briceland, Humboldt County, in 1894 furnished the town with natural gas for many years. In 1901, a well was completed in Solano County and supplied gas to the towns of Suisun and Fairfield (Stalder, 1943, p. 79).

Although the first discovery in California of wet gas with oil occurred in Pico Canyon near Newhall in Los Angeles County in 1870, not until 1907 was oil-well gas commercially distributed. In that year, gas from the Orcutt (Santa Maria) oil field was used to supply Santa Maria and nearby towns (Masser, 1923, p. 18).

The natural-gas industry began to develop rapidly after 1909 when oil and gas were discovered in the





FIGURE 1.



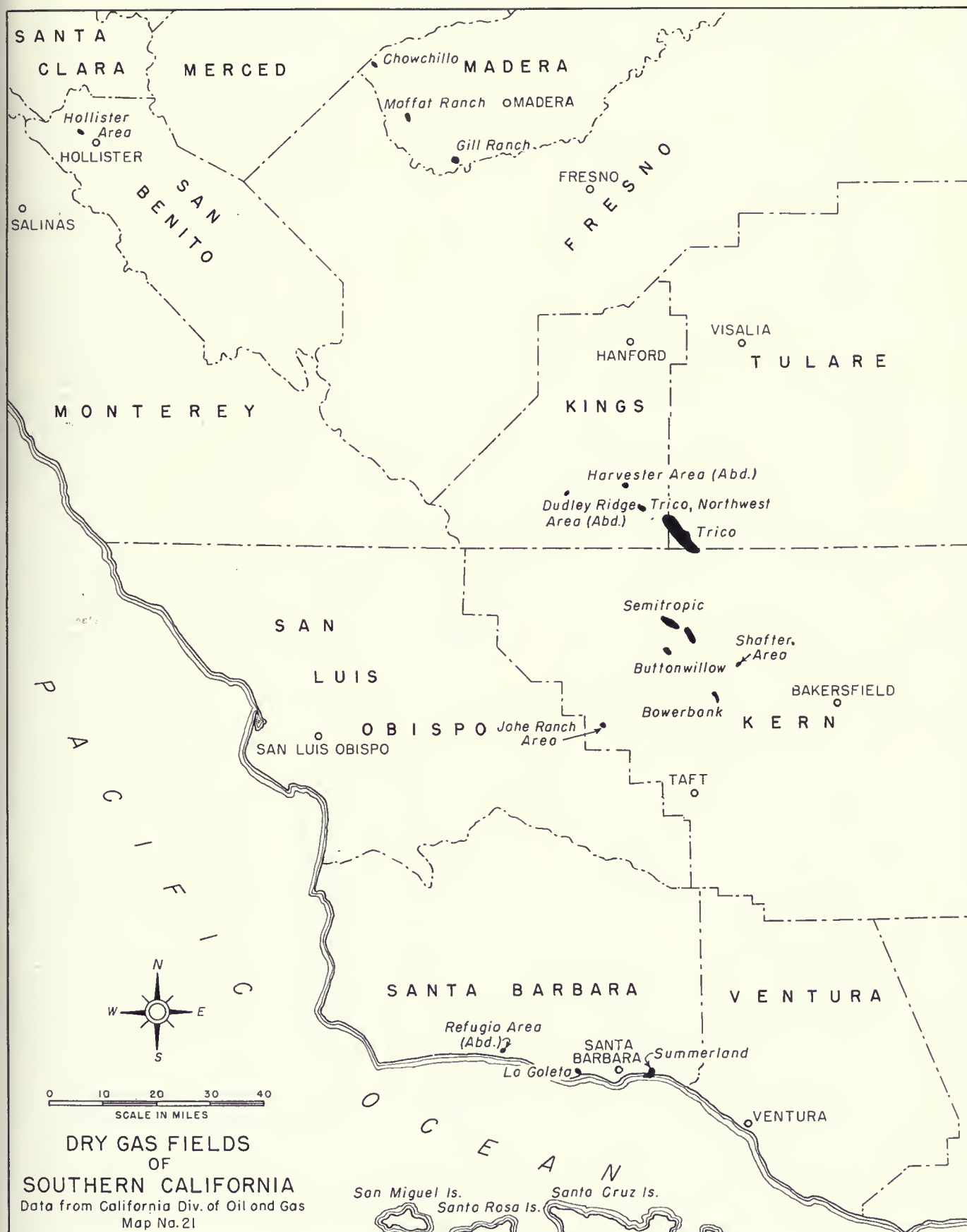


FIGURE 2.



Table 2. Principal dry gas fields—discovery and geologic data through 1954.\*

County	Field	Discovery year	Company	Well	Producing depth	Initial production Mcf/day	Structure or trap**	Geologic age of producing formation
Alameda	Hospital Nose (Livermore) area	52	Texas	Hancock-Signal-Wente (NCT-1) 1	5,180 & 5,280	150	S	Miocene
Butte	Chico	44	Richfield	Chico 1	4,390	3,500	--	Cretaceous
	Durham	46	Standard	Donohoe Fee 1	2,176	10,937	A	Eocene
	Llano Seco area	54	Humble	Parrott Inv. Co. 2	3,300	4,000	A(?)	Cretaceous
	Wild Goose	51	Honolulu	Honolulu-Humble-Wild Goose 1	3,260 & 3,314	4,020	A	Paleocene or Cretaceous (Kione)
Colusa	Colusa***	43	General	Capital 1	2,940	3,200	A	Cretaceous
	Moon Bend area	54	Humble	Steidlmayer 3	1,415	1,700	A(?)	Cretaceous
	Princeton	53	Richard S. Rheem	Southam 1	2,230	2,850	--	Cretaceous (Kione)
Contra Costa	Rio Vista (see Solano County)							
Glenn	Afton	44	Richfield	Afton Comm. 1-1	2,660	5,700	A	Cretaceous
	Beehive Bend	53	Sunray	Estes 1	3,665	3,900	S(?)	Cretaceous
	Beehive Bend NW area	54	Richard S. Rheem	Zumwalt 1	5,944	6,300	S(?)	Cretaceous
	Ord Bend	43	Superior	Knight 1	3,664	5,040	A	Cretaceous
	Willows	38	Ohio	Willard 1-A	2,240	5,000	A	Cretaceous
Humboldt	Tompkins Hill (Eureka)	37	Texas	Eureka 2	4,862	500	A	Pliocene
Kern	Bowerbank	42	Texas	S. P. 47-15	4,262	10,000	A	Pliocene
	Buttonwillow	27	Milham Expl.	Kern 1-A	2,648	11,700	A	Pliocene
	Johe Ranch area	54	Union	Hancock 36-7	1,420	4,000	S(?)	Miocene
	Semitropic	35	Standard	Hill 1	3,200	107,000	A	Pliocene
	Shafter area	54	Tidewater	Loepp 63-18	4,305	5,400	S(?)	Pliocene
	Trico (partly in Kings and Tulare Counties)	34	Trico	Well 2	2,476	Blew out	A	Pliocene
Kings	Dudley Ridge area***	20	Pacific Oil & Gas	Well 1	2,085	27+	F or A	Pleistocene?
	Harvester area (of NW Trico)***	50	Shell	Harvester Unit 1-1	2,805	4,150	FS	Pliocene
	Trico, Northwest	44	Standard	Cutter Unit 1	3,510	14,388	A	Pliocene
Madera	Chowchilla	34	Pure	Chowchilla 1	8,060	18,000	A	Cretaceous
	Gill Ranch	43	Texas	Gill 38-16	4,485	11,000	FA	Eocene
	Moffat Ranch	43	Texas	Moffat 1-7	3,935	6,500	A	Eocene
Sacramento	Freeport	52	Standard	Simms Comm. 1	5,788 & 5,875	9,784	--	Cretaceous
	Rio Vista (see Solano County)							
	River Island	50	Brazos	River Islands Land Co. 1	4,170	4,805	F	Eocene
	Thornton (partly in San Joaquin County)	43	Amerada	Housken Comm. 1	3,380	6,850	A	Eocene
San Benito	Hollister area (Lomerias Ranch)	52	Balken & Krug	Ferry-Morse 1	2,400	3,000-5,000 (Blew out initially)	S(?)	Pliocene
San Joaquin	Galt	43	Bankline	Community 1-1	2,340	7,765	A	Eocene
	Lodi	43	Amerada	Lodi Comm. 9-1	2,270	7,200	A	Eocene
	McDonald Island	36	Standard	McDonald Island Farms 1	5,227	26,647	A	Paleocene
	Roberts Island	42	Standard	Woods Comm. 2-1	5,254	5,613	A	Paleocene
	Tracy	35	Amerada	F. D. L. 2	4,063	35,000	A	Cretaceous
	Vernalis (partly in Stanislaus County)	41	Standard	Blewett 1	3,872	10,000	A	Cretaceous
Santa Barbara	La Goleta	29	General	More 1	4,273	17,000	FA	Miocene
	Refugio area***	47	Rothschild	Orella 1	2,500	5,000	FA	Miocene
	Summerland	48	Standard	Williams 1	3,700	2,155	A	Oligocene
Solano	Cache Slough	45	Standard	Cal. Pack. Corp. 2	4,795	14,867	A	Eocene
	Denverton area***	48	Honolulu	McCormick Est. 1	2,150	845	A	Cretaceous
	Honker area***	44	Standard	Honker Comm. 1-A	7,220	3,200	FA	Eocene or Paleocene
	Kirby Hill	45	Shell	Lambie 1-A	2,316	3,980	FA	Eocene
	Kirby Hill, North	53	Shell	Unit B-1	3,555	5,000	--	Eocene
	Liberty Cut	53	Arcady	Fahn 1	4,138	2,000	--	Eocene
	Maine Prairie	45	Amerada	Wineman 1	4,790	18,997	FA	Eocene
	Millar	44	Amerada	Starkey Fee 1	4,600	22,750	A	Eocene
	Potrero Hills area***	38	Richfield	Potrero Hills 1	3,265	1,500	A	Cretaceous
	Rio Vista (partly in Sacramento and Contra Costa Counties)	36	Amerada	Emigh 1	4,278	50,000	FA	Eocene
	Suisun Bay	44	Standard	Suisun Comm. 3	3,640 & 3,909	7,350	FA	Eocene
	Winters (partly in Yolo County)	46	Shell	McCune 1	5,240	11,000	A	Cretaceous



Table 2. Principal dry gas fields—discovery and geological data through 1954.\*—Continued.

County	Field	Discovery year	Company	Well	Producing depth	Initial production Mcf/day	Structure or trap**	Geologic age of producing formation
Sutter	Marysville Buttes (Sutter Buttes)	33	Buttes Oilfields	Well 1	2,727	3,425	Complex	Cretaceous
Tehama	Corning	44	Superior	Saldubehere 1	1,504	17,676	A	Pliocene
	Corning, South	51	Buttes Oilfields	Saldubehere-Buttes A	1,590	10,000	A	Pliocene
Yolo	Dunnigan Hills	46	Texas	Hermle 1	2,620	3,030	A	Cretaceous
	Fairfield Knolls	37	Standard	Hooper 1	3,700	7,340	A	Cretaceous
	Pleasant Creek	48	Shell	Unit 3-1	2,818	9,550	A	Paleocene or Cretaceous
	Sycamore Slough area	53	Signal	Signal-Monterey-Reclamation 1	3,724	4,100	--	Eocene

\* Sources of data: Petroleum World Annual Reviews 1949 and 1954; California Division of Oil and Gas Summary of Operations, 1954 and prior; California Division of Mines publications.

\*\* A = Anticline or dome. F = Fault. S = Stratigraphic.

\*\*\* Abandoned.

Buena Vista Hills field (now part of the Midway-Sunset field). Natural gas was subsequently piped 40 miles to Bakersfield in 1910 and about 115 miles to Los Angeles in 1913. Thereafter, the natural-gas industry of southern California expanded greatly with the development of the West Coyote field in 1914-17, Elk Hills field in 1919, Huntington Beach, Long Beach, and Santa Fe Springs fields in 1922-24 and Ventura Avenue field in 1925. In 1927, dry gas was found at Buttonwillow, Kern County. This was the first significant discovery in California of dry gas not associated structurally with an oil field. This discovery was soon overshadowed when the Kettleman Hills field was brought in the following year. Gas piped from Kettleman Hills in 1929 was the first natural gas to reach San Francisco and was the beginning of state-wide gas distribution (Bauer, 1943, pp. 33-36).

The first high-pressure gas well in northern California was brought in at Marysville Buttes, Sutter County, in 1933 by Buttes Oilfields, Inc. The well produced an initial 3,425 thousand cubic feet per day from a depth of 2,727 feet. In June 1936, the Rio Vista gas field was discovered by Amerada Petroleum Corporation. The discovery well was brought in at 50,000 thousand cubic feet per day from the Emigh sand of Eocene age at a depth of 4,485 feet. Rio Vista has led all fields in the production of natural gas since 1943 and in 1954 yielded approximately 13 percent of the state's total production and well over half of the dry gas produced.

An intensive search for gas was initiated in the late 1930s and since then about 35 or 40 dry gas fields have been discovered in the Sacramento and northern San Joaquin Valleys. Most of these fields have proved to be disappointingly small and have added little to the reserves of California.

**Recent Discoveries of Gas Fields.** Between 1951 and 1954, fifteen new gas fields were discovered in California, twelve in the Sacramento Valley and three in the San Joaquin Valley. Of these, only two fields, Wild Goose and Beehive Bend, now appear to be of real significance. The Wild Goose field was discovered in August 1951, when Honolulu Oil Corporation's well Honolulu-Humble-Wild Goose 1 was completed and flowed 4,020 thousand cubic feet of gas per day from

depths of 3,260 and 3,292 feet. In 1954, Wild Goose was the fourth largest producing gas field in the state and had the third largest reserves. The Beehive Bend field was discovered in May 1953 by General Petroleum Corporation when their well Estes 1 blew in at 3,900 thousand cubic feet per day from a depth of 3,665 feet. As of November 1955, twenty wells and pipeline facilities had been completed and the Beehive Bend field was scheduled to go on production for the first time in the winter of 1955-56 (Stockman, 1955, p. 38). Discoveries of gas-yielding oil fields are not discussed herein, as oil field discovery data are given in the section on petroleum.

In spite of intensive exploration and numerous discoveries, no major dry gas fields have been found in California since Rio Vista in 1936.

Table 3. Marketed production<sup>1</sup> of natural gas in California, 1906-54.

(Data from U. S. Bureau of Mines.)

Year	Estimated value at wells (1000 dollars)	Production (million cu. ft.)	Year	Estimated value at wells (1000 dollars)	Production (million cu. ft.)
1906	135	153	1931	21,446	305,930
1907	168	230	1932	17,126	263,484
1908	308	479	1933	16,690	259,799
1909	447	2,324	1934	18,739	268,122
1910	477	2,764	1935	19,916	284,109
1911	801	6,390	1936	20,858	320,406
1912	1,134	9,355	1937	21,699	329,769
1913	1,883	11,035	1938	21,778	315,168
1914	2,911	17,829	1939	21,529	348,361
1915	4,069	21,891	1940	19,604	351,950
1916	5,440	31,643	1941	22,437	374,905
1917	6,817	49,427	1942	26,662	403,968
1918	7,952	39,719	1943	29,800	457,757
1919	9,366	55,607	1944	32,330	502,017
1920	12,528	66,041	1945	30,147	502,442
1921	16,496	75,942	1946	36,056	487,904
1922	7,612	84,580	1947	57,284	560,510
1923	8,543	131,434	1948	64,803	570,954
1924	14,227	189,692	1949	64,731	550,903
1925	14,084	187,789	1950	66,449	558,398
1926	16,803	204,915	1951	82,745	566,751
1927	19,431	212,364	1952	86,414	517,450
1928	21,692	246,215	1953	104,675	531,346
1929	29,054	342,314	1954	104,289	507,289
1930	25,210	334,789			

<sup>1</sup> Excludes gas used for repressuring and gas (mostly residue gas) blown to air.



Table 4. Natural gas withdrawals and reserves in California by fields.<sup>a</sup>  
(Thousands of cubic feet.)

County	Field	Net gas withdrawn in 1954	Cumulative production of gas through 1954†	Gas reserves as of Jan. 1, 1955	County	Field	Net gas withdrawn in 1954	Cumulative production of gas through 1954†	Gas reserves as of Jan. 1, 1955
Alameda	Hospital Nose area, gas	9,424	11,377	*	Kern—	McKittrick	64,530	5	*
Butte	Chico gas	62,414	922,746	214,699	Continued	Gas zone	131,796	5	*
	Durham gas	682,627	3,143,617	*		Midway-Sunset <sup>b</sup>	11,483,852	5	10,981,987
	Wild Goose gas	4,156,551	8,433,172	79,316,828		Buena Vista gas zone	610,414	5	3,373,613
Colusa	Princeton gas	4,094	4,094	*		Mount Poso	55,560	1,609,505	81,489
Fresno	Burrel	201,123	1,028,533	678,467		Mountain View	1,576,433	62,274,428	6,518,567
	Camden area	18,290	66,312	*		Paloma, all zones	30,640,803	183,923,482	477,545,936
	Cantua Creek area	138,016	764,624	*		Gas zone	23,451	3,145,284	
	Cheney Ranch area	0	309,325	*		Symons zone	351,702	6,988,558	
	Coalinga	782,118	212,980,841	9,134,882		Paloma zone	30,265,650	171,789,640	
	Coalinga, East Extension	10,478,880	226,536,671	414,236,944		Pleito Creek	71,422	148,765	*
	Gujarral Hills	4,096,576	32,380,047	18,975,804		Poso Creek	130,985	1,742,065	193,517
	Helm	3,741,557	48,530,347	169,669,424		Rio Bravo	2,107,444	58,667,731	139,638,476
	Jacalitos	1,111,626	17,909,254	29,350,164		Rosedale	645,727	1,288,427	*
	Pleasant Valley	330,247	10,153,613	12,543,968		Rosedale Ranch	397,970	740,613	*
	Raisin City	562,612	12,585,853	5,737,388		Round Mountain	46,858	517,567	195,496
	Riverdale	919,831	20,035,514	19,361,858		Semitropic gas	60,190	14,073,667	9,356,015
	San Joaquin	5,916	228,474	225,884		Strand			
Glenn	Afton gas	165,381	3,348,985	2,628,192		Main area	75,765	4,287,722	9,222,006
	Beehive Bend gas	0	0	*		East area	89,101	1,824,416	3,371,782
	Ord Bend gas	484,586	6,170,654	523,539		Tejon	682,428	4,810,091	931,188
	Willows gas	97,001	294,088	*		Tejon Flats area	745	1,882	*
Humboldt	Eureka gas	1,914,527	14,617,162	19,131,663		Tejon Hills	163,098	828,883	*
	Petrolia area	0	0	*		Gas zone	4,996	21,219	*
Kern	Ant Hill	6,228	216,543	15,598		Temblor area	0	0	*
	Antelope Hills	436,267	3,840,737	5,205,116		Temblor Ranch	0	0	*
	Antelope Hills, North	44,683	288,558	*	Kings	Ten Section	1,134,797	142,593,209	66,193,461
	Bates area	0	0	*		Trico gas <sup>c</sup>	7,862,645	89,462,737	165,724,395
	Belgian Anticline	18,694,246	52,546,367	81,305,754		Union Avenue	59,545	792,879	*
	Bellevue	203,061	1,315,788	2,341,054		Wasco	229,847	2,947,373	1,070,153
	Belridge, North	16,621	11,208,471	11,529		Welcome Valley	0	0	*
	Shallow zone	16,664	56,215,465	23,916,508		Wheeler Ridge	2,694,248	8,145,743	14,207,040
	Temblor zone	16,664	56,215,465	23,916,508		Kettleman Middle Dome <sup>d</sup>	319,962	22,840,826	6,370,038
	R zone	6,616,696	81,367,041	2,383,304		Kettleman North Dome	38,203,470	2,311,339,834	1,300,800,179
	64 zone	2(3,010,102)	319,605,375	83,745,050		Pyramid Hills	19,332	115,499	*
	Y zone	2(536,787)	3,900,894	2,473,974		Trico, Northwest, gas	669,669	1,604,993	*
	Belridge, South	666,642	301,056	301,056	Los Angeles	Aliso Canyon	2,580,144	26,826,992	44,656,414
	Blackwells Corner	4,040	69,905	204,320		Alondra area	55,845	815,089	3,601,800
	Bowerbank gas	279,929	6,210,566	31,178,414		Bandini area	386,239	403,839	*
	Buttonwillow gas	9,050	33,421,355	20,950		Beverly Hills	31,616	5	*
	Calders Corner area	30,445	311,722	4,508		Canoga Park area	0	0	*
	Canal	985,610	20,229,268	29,747,929		Castaic Hills	2,919,581	8,167,034	6,253,609
	Canfield Ranch	1,116,623	5,845,822	1,448,975		Castaic Junction	1,216,386	3,115,432	2,614,289
	Chico-Martinez area	0	0	*		Del Valle	6,535,550	64,481,703	12,062,401
	Coles Levee, North	2(117,535)	2(6,804,720)	373,459,688		Domingues	4,418,619	327,482,627	48,254,338
	Gas zone	104,484	64,524,493	5,223,614		El Segundo	7,965	5	248,804
	Coles Levee, South	2,160,023	49,849,903	544,845,838		Gas zone	149,993	5	8,613,387
	Gas zone	1,958,474	27,703,594	3,041,526		Elizabeth Canyon area	407	5	5,666,233
	Comanche Point	0	25	*		Honor Rancho	978,110	2,929,662	16,951
	Cymric	1,518,662	5	16,548,322		Horse Meadows area	5,833	16,951	5,428,065
	Devils Den	94,621	155,461	*		Howard Townsite	1,722,395	11,880,784	77,737
	Edison	5,134,752	24,852,744	27,949,730		Hyperion area	8,249	8,249	12,460,478
	Elk Hills, all zones	253,367,427	580,381,259	580,381,259		Inglewood	4,007,772	143,116,414	10,425
	Gas zone	2(350,648)	301,819,828	2,908,290		La Mirada area	2,382	10,425	*
	Upper zone	21,079,376	215,103,841	36,047		Las Lajas area	1,095	4,659	*
	Stevens zone	142,683	3,080,459	*		Lawndale	138,204	5,991,293	3,428,773
	Carneros zone	63,050	363,299	*		Leffingwell area	667,280	1,419,947	*
	Fruitvale	1,450,330	13,830,975	107,349,967		Long Beach	6,683,975	993,094,831	55,490,699
	Greeley	1,487,246	48,574,155	107,349,967		Long Beach Airport area	702,916	702,916	*
	Greenacres area	0	0	*		Los Angeles City	0	5	*
	Jasmin	0	0	*		Los Angeles, East	302,725	5,516,071	4,483,929
	Johe Ranch area, gas	0	0	*		Mission area	39,829	63,484	*
	Kern Bluff	0	0	*		Montebello	2,573,863	179,088,719	10,054,550
	Kern Front	214,667	11,693,435	2,582,326		Newhall	36,409	5	133,587,693
	Kern River	2,524	2,432,222	36,047		Newhall-Potrero	1,818,903	27,595,784	21,072,776
	Los Lobos	88,552	122,579	*		Oak Canyon	705,893	9,096,048	*
	Lost Hills	1,959,298	5	488,203		Placerita	188,252	5,149,608	*
	Lost Hills, Northwest area	3,524	4,909	*		Playa del Rey	590,091	5	2,333,397
	McDonald Anticline	214,083	1,695,255	*		Playa del Rey Hills	2(1,781,400)	5	5,038,344
						Gas storage	1,415,141	40,083,072	8,100,998
						Potrero	1,657,516	138,130,257	3,939,432
						Rosecrans	342,662	16,096,879	1,649,188
						Rosecrans, South			



Table 4. Natural gas withdrawals and reserves in California by fields.<sup>a</sup>—Continued.  
(Thousands of cubic feet.)

County	Field	Net gas withdrawn in 1954	Cumulative production of gas through 1954†	Gas reserves as of Jan. 1, 1955	County	Field	Net gas withdrawn in 1954	Cumulative production of gas through 1954†	Gas reserves as of Jan. 1, 1955
Los Angeles—Continued	Salt Lake	0	5	*	Santa Barbara—Continued	Cuyama, South	866,257	29,675,843	249,829,157
	Sansinena	2,551,393	7,358,362	21,929,054		Elwood	1,356,662	83,555,083	4,393,338
	Santa Fe Springs	5,623,319	751,601,225	72,604,907		Jesus Maria area	0	0	*
	Seal Beach <sup>9</sup>	5,424,224	135,779,910	25,511,580		La Goleta gas	1(1,668,179)	7,473,909	41,962,548
	Torrance	1,732,484	99,442,265	3,722,517		Lompoc	1,325,798	7,886,884	4,742,040
	Turnbull	23,782	513,225	149,038		Mesa	0	7,547	*
	Walnut area	0	0	*		Oreutt	2,176,892	236,100,999	12,985,509
	Whittier	272,620	8,055,355	851,231		Russell Ranch	3,097,633	15,397,347	63,040,653
	Gas storage <sup>1</sup>	2(344,767)	(1,124,325)	1,124,325		Santa Maria Valley <sup>14</sup>	6,927,976	133,589,641	12,372,472
	Whittier Heights, North, area	0	0	*		Summerland	0	0	*
	Wilmington	34,018,746	654,120,007	382,974,290		Gas zone	179,820	1,662,115	*
						Zaca	499,862	868,037	*
Madera	Chowchilla gas	543,230	734,804	19,507,770	Santa Clara	Moody Gulch	0	44,000	*
	Gill Ranch gas	2,117,391	23,826,508	15,121,472		Sargent <sup>15</sup>	0	275,000	*
	Moffat Ranch gas	485,814	2,377,568	*	Solano	Cache Slough gas	766,562	8,463,657	3,104,070
Monterey	San Ardo	5,045,917	7,584,366	*		Kirby Hill gas	2,465,941	25,714,621	16,135,129
Orange	Belmont Off-Shore area	728	7,695	*		Kirby Hill, North, gas	0	3,167	*
	Brea-Olinda <sup>10</sup>	9,934,260	299,846,590	48,385,741		Liberty Cut gas	0	400	*
	Gas storage <sup>1</sup>	83,354	1,285,367	205,781		Maine Prairie gas	2,477,583	12,573,643	12,632,439
	Coyote, East	2,424,432	27,530,476	19,859,840		Millar gas	453,668	8,880,957	11,889,147
	Coyote, West <sup>11</sup>	3,132,983	230,308,477	33,644,207		Rio Vista gas <sup>16</sup>	67,477,766	1,634,260,032	1,408,684,048
	Huntington Beach	15,871,689	515,972,934	102,408,817		Suisun Bay gas	2,171,898	17,386,621	53,373,377
	Kraemer	50,825	435,486	174,987		Winters gas <sup>17</sup>	1,778,864	9,370,207	4,107,886
	Newport	0	0	*	Sonoma	Petaluma area	0	0	*
	Newport, West	164,796	5,192,884	533,100		Gas zone	0	32,281	*
	Gas zone	0	147,814	*	Sutter	Marysville Buttes gas	950,495	13,479,814	11,949,890
	Olive area	30,000	30,000	*	Tehama	Corning gas	457,938	457,938	26,257,851
	Richfield	2,423,213	148,753,647	3,966,118		Corning, South, gas	69,216	69,216	4,590,714
	San Clemente area	446	446	*	Tulare	Deer Creek area	0	0	*
	Sunset Beach area	1,135	1,135	*		Terra Bella area	0	0	*
	Talbert area	0	4,481	*	Ventura	Bardsdale	1,962,658	51,592,340	6,177,151
	Yorba Linda	29,237	923,043	372,386		Conejo	0	0	*
Sacramento	Freeport gas	316,149	933,367	*		Fillmore area	139,664	139,664	*
	River Island gas	4,976,989	9,454,880	7,966,698		Montalvo, West	1,934,298	7,765,767	7,834,233
	Thornton gas <sup>12</sup>	2,841,366	24,556,751	3,018,367		Oakridge	715,656	1,820,317	4,107,090
San Benito	Bitterwater area	0	0	*		Ojai	152,312	0	*
	Ciervo area	0	4,557	*		Oxnard	542,642	41,933,158	*
	Hollister area, gas	23,771	94,030	*		Piru	81,841	1,416,673	*
	Lomerias area	0	0	*		Ramona <sup>18</sup>	2,604,682	18,218,064	12,394,704
	Vallejos area	0	0	*		Rineon	6,078,526	72,945,119	30,638,267
San Bernardino	Chino-Soquel area	243	1,042	*		San Miguelito	11,511,649	102,909,336	107,017,906
San Joaquin	Galt gas	90,854	1,019,445	*		Santa Paula	283,991	0	*
	Lodi gas	865,773	7,192,690	10,257,798		Sespe	14,852	0	*
	McDonald Island gas	3,552,512	117,914,799	64,020,201		Shiells Canyon	523,044	37,229,118	1,595,613
	Roberts Island gas	367,604	5,030,162	969,838		Simi	6,697	0	*
	Tracy gas	35	13,775,969	9,029,411		South Mountain	7,117,025	101,202,955	23,622,829
	Vernalis gas <sup>13</sup>	194,556	8,916,780	4,297,120		Tapo Canyon, South	281,234	475,714	880,481
San Luis Obispo	Arroyo Grande	0	18,464	*		Temescal	106,458	4,240,837	1,006,914
	Gnadalupe	605,862	808,893	*		Torrey Canyon	1,152,348	7,136,972	*
	Morales	125,636	969,598	*		Ventura Avenue	57,175,330	1,334,622,556	360,719,439
	Taylor Canyon area	11,145	79,893	*	Yolo	Dunnigan Hills gas	1,244,812	5,614,539	7,381,391
Santa Barbara	Barham Ranch area	0	0	*		Fairfield Knolls gas	0	2,521,805	*
	Capitan	272,372	11,360,012	1,837,628		Pleasant Creek gas	351,983	3,138,906	*
	Casmalia	216,780	4,837,605	*		Sycamore Slough area, gas	250	2,750	*
	Cat Canyon	3,650,438	26,279,856	17,619,562		Grand totals	512,316,141	13,793,152,249	8,703,153,558
	Coal Oil Point area	0	17,672	*					
	Cuyama, Central, area	3,272	6,410	*					

<sup>a</sup> Data from California Division of Oil and Gas.

<sup>\*</sup> No reserves estimated because of lack of data, or because they are insufficient to justify pipeline connections.

<sup>†</sup> First gas production reports were filed in 1929. Figures for earlier years were estimated.

<sup>1</sup> Storage only.

<sup>2</sup> Considered to be returned from or delivered to underground storage. Parentheses indicate negative figures due to storage. All figures are net.

<sup>3</sup> Not included in totals.

<sup>4</sup> Revised figure.

<sup>5</sup> Figures have not been compiled. Totals include only those fields for which entries have been made.

<sup>6</sup> Includes the portion of Midway-Sunset field in San Luis Obispo County.

<sup>7</sup> Includes the portion of Trio gas field in Kings and Tulare Counties.

<sup>8</sup> Includes the portion of Kettleman North Dome field in Fresno County.

<sup>9</sup> Includes the portion of Seal Beach field in Orange County.

<sup>10</sup> Includes the portion of Brea-Olinda field in Los Angeles County.

<sup>11</sup> Includes the portion of West Coyote field in Los Angeles County.

<sup>12</sup> Includes the portion of Thornton gas field in San Joaquin County.

<sup>13</sup> Includes the portion of Vernalis gas field in Stanislaus County.

<sup>14</sup> Includes the portion of Russell Ranch field in San Luis Obispo County.

<sup>15</sup> Reactivated field.

<sup>16</sup> Includes the portion of Rio Vista gas field in Sacramento and Contra Costa Counties.

<sup>17</sup> Includes the portion of Winters gas field in Yolo County.

<sup>18</sup> Includes the portion of Ramona field in Los Angeles County.



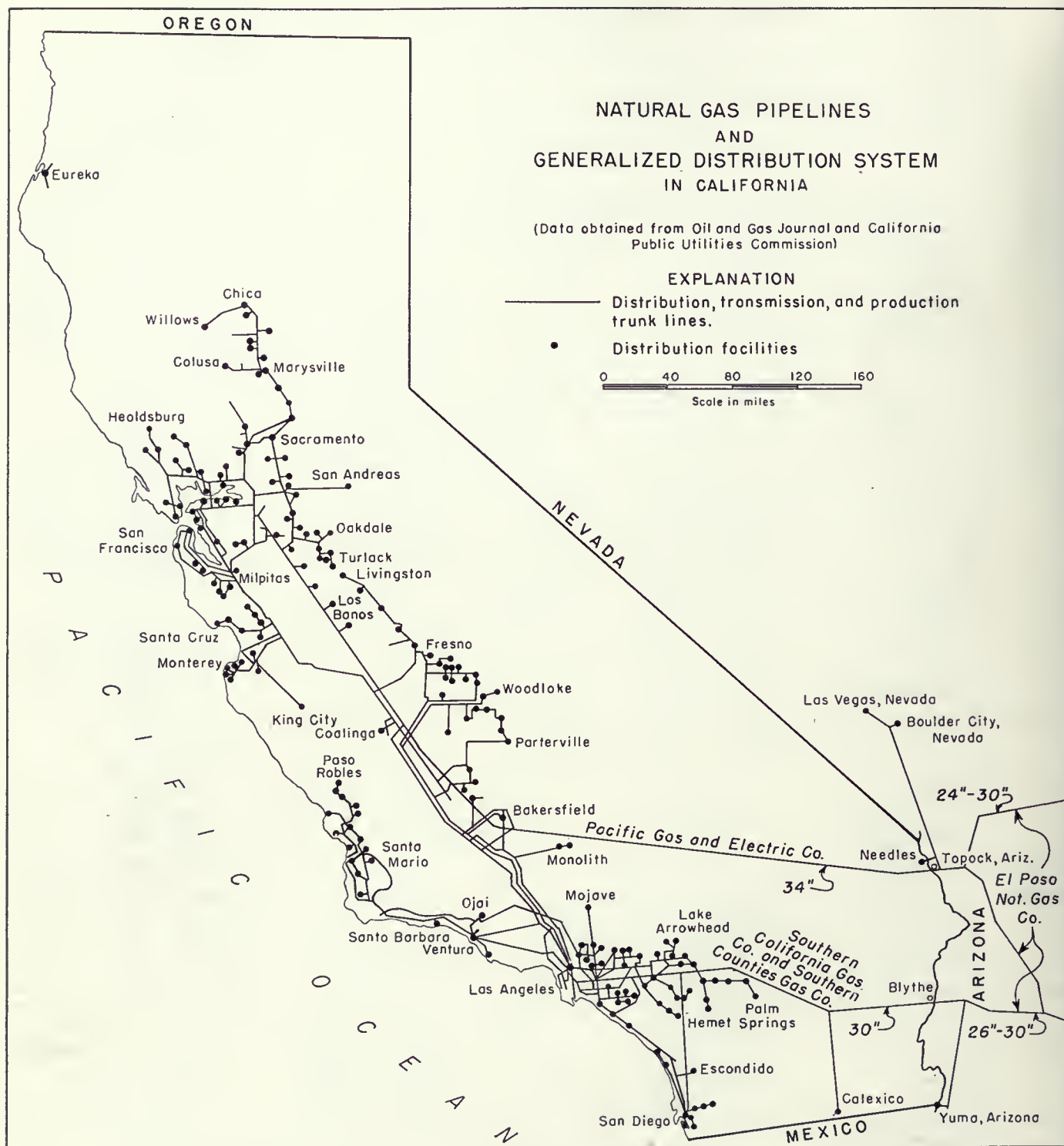


FIGURE 3.

*Production.* According to the U.S. Bureau of Mines, California's marketed production of natural gas in 1954 was 507,289,000 thousand cubic feet with an estimated value, before distribution, of \$104,502,000. Compared with the preceding year, the volume decreased nearly 5 percent although the value was about the same. Preliminary figures indicate that a moderate increase in

production will be recorded in 1955. However, substantial increases in production in the future cannot be expected without further important discoveries.

*Reserves.* The small additions to the state's reserves of natural gas have come mainly from extensions and revisions in known oil and gas fields, and to a lesser extent from discoveries of new fields and new pools in



Table 5. Consumption of natural gas in California—1948-53.  
(Data from U. S. Bureau of Mines.)

Uses	1948	1949	1950	1951	1952	1953
Residential (heating and some cooking)						
Volume <sup>1</sup> .....	157,327	174,811	179,351	196,819	228,390	223,649
Number of consumers.....	2,336,110	2,508,894	2,681,814	2,869,904	3,007,954	3,163,000
Average value at point of consumption <sup>2</sup> .....	61.2	61.3	66.4	67.8	69.9	72.9
Commercial (heating)						
Volume <sup>1</sup> .....	70,875	77,800	72,707	72,676	79,757	78,790
Number of consumers.....	203,820	190,960	192,136	200,568	235,128	240,000
Average value at point of consumption <sup>2</sup> .....	39.5	39.7	41.4	45.4	50.6	55.7
Industrial (fuel and some chemical)						
Volume <sup>1</sup> .....						
Field plants and drilling.....	132,445	130,218	139,584	158,050	154,654	159,349
Petroleum refineries.....	73,623	47,527	56,671	77,764	75,696	81,220
Electric power generation.....	61,178	65,342	78,322	83,141	74,287	117,559
Other industrial <sup>3</sup> .....	122,167	123,625	157,289	199,398	179,736	201,676
Total industrial.....	389,413	366,712	431,866	518,353	484,373	559,804
Average value at point of consumption <sup>2</sup> .....	21.2	19.6	18.9	21.3	23.4	26.2
Total consumption						
Volume <sup>1</sup> .....	617,615	619,323	683,924	787,848	792,520	862,243
Average value at point of consumption <sup>2</sup> .....	33.5	33.9	33.7	35.1	39.5	39.9

<sup>1</sup> Millions of cubic feet.

<sup>2</sup> Cents per 1,000 cubic feet.

<sup>3</sup> Portland cement, carbon black, etc.

old fields. These additions have not kept pace with net withdrawals in recent years and, as a result, California's natural-gas reserves have steadily declined. For example, total reserves on January 1, 1955, were 8,703,153,558 thousand cubic feet compared to 9,071,542,403 on January 1, 1954, a decrease of 4 percent (Musser, 1954). Since 1950 the state's reserves have declined about 10 percent.

**Processing.** Before natural gas is ready for consumption, it is usually processed to remove oil, water, dust and other impurities and is then odorized so that leakage can be detected. Nearly all of the wet gas is processed at natural-gasoline and cycle plants for removal of the valuable natural gasoline and liquefied petroleum gases (see the section on natural-gas liquids for a more detailed discussion). Many operators find it necessary to remove hydrogen sulfide ( $H_2S$ ), a very toxic gas, which may be utilized as a byproduct to manufacture elemental sulfur or sulfuric acid. Carbon dioxide ( $CO_2$ ), an inert gas, decreases the heating value of the natural gas. At least one operator advantageously removes the carbon dioxide as a byproduct for the manufacture of dry ice and at the same time has increased the heating value of the natural gas.

**Utilization and Distribution.** The use of natural gas, in the rest of the United States as well as in California, has grown tremendously in the last several years. In 1954, natural gas supplied the United States with 25 percent of its total energy requirements as compared to 4 percent in 1920 and 14 percent in 1947. California consumed nearly 11 percent of the natural gas utilized in the United States in 1953 and was second only to Texas. The natural gas distribution system, an integral part of the natural-gas industry, has expanded at a rate proportional to that of the industry. Natural-gas pipeline mileage in the state has increased from 22,000 in 1935 to 40,800 in 1954, with the most rapid growth coming in the last 7 years. In 1954, California had 340

miles of field and gathering mains, 4,820 miles of transmission mains, and 35,640 miles of distribution mains, accounting for nearly 10 percent of the nation's natural-gas pipelines.

The uses of natural gas can be conveniently broken down into three major groups—residential, commercial, and industrial. Nearly all of the gas utilized by residential and commercial consumers is for heating purposes. In industry, natural gas is used primarily as a fuel, but some is also used as a chemical raw material.

Residential consumers of natural gas in 1954 numbered 3,303,000, an increase of 7 percent over the previous year. In 1953, residential consumption amounted to 26 percent of the total gas consumed in the state. The demand for residential gas for space heating, cooking, and water heating will continue to be high during the next few years as new homes are constructed. In the Los Angeles area during 1954, for example, 92.9 percent of all new homes were equipped with gas ranges, 98.8 percent with gas water heaters, and 99.5 percent with gas heating equipment (Wells Fargo Bus. Rev., 1955).

Commercial use of natural gas primarily includes the space heating of all types of building structures other than residential. Consumption in this classification has increased very little during the last few years, although the number of consumers in California increased substantially over the same period of time. Commercial heating amounted to 9 percent of the total consumption in the state in 1953.

Although industrial consumption of natural gas has fluctuated somewhat during the last several years, a strong over-all increase has been recorded. U. S. Bureau of Mines statistics show that gas utilized in California industry increased by 44 percent from 1948 to 1953. Natural gas in industry is used mostly for fuel, with small amounts used as a chemical raw material. Gas, as an industrial fuel, is utilized mainly in field plants and well drilling, refineries and pump stations, electric power generation, portland cement plants, natural-gas



Table 6. Number of natural gas consumers in California on December 31, 1936-54.\*  
(Thousands of consumers.)

Year (On Dec. 31)	Residential	Commercial	Total
1936	1,427	90	1,517
1937	1,483	90	1,573
1938	1,541	90	1,631
1939	1,611	92	1,703
1940	1,693	93	1,786
1941	1,799	103	1,902
1942	1,867	105	1,972
1943	1,884	145	2,029
1944	1,922	163	2,085
1945	1,967	169	2,136
1946	2,034	181	2,215
1947	2,186	184	2,370
1948	2,336	204	2,540
1949	2,509	191	2,700
1950	2,682	192	2,874
1951	2,870	200	3,070
1952	3,008	235	3,243
1953	3,163	240	3,403
1954	3,303	256	3,559

\* Data from U. S. Bureau of Mines.

pipeline compressors, ceramic and glass manufacture, food processing, textile manufacture, metal fabrication, and primary iron and steel industries.

Natural gas used in the chemical industry of California amounts to a small percentage of the total gas consumed in the state. However, the ultimate value of the chemical products derived from gas is many times higher than the value of gas when it is used as a fuel. By processing the methane and ethane components of natural gas, chemical manufacturers obtain a myriad of chemical intermediates and end products. A few of the better known products derived from methane are ammonia, carbon dioxide, methyl alcohol, nitric acid, urea, formaldehyde, pharmaceuticals, carbon tetrachloride, acetylene, various resins, and carbon black. The most important products derived from ethane are, polyethylene, ethyl alcohol, ethylene glycol, tetraethyl lead, acrylonitrile, dacron, styrene, detergents, and acetic acid (Crockett, 1955, pp. 165-173, and Cattell et al., 1955, pp. 6-12). Not all of the above products are manufactured in California.

The total value of natural gas at points of consumption for California in 1953 amounted to \$343,682,000, an increase of nearly 10 percent over the preceding year. Residential, commercial, and industrial values were \$162,967,000, \$43,907,000, and \$136,808,000, respectively. Large differences in rates exist among the three classes of consumers. Highest rates are paid by residential users. Commercial users, because of the larger volumes of consumption by individual consumers, have lower rates. Industrial users pay the lowest rates because they use large volumes at times of lowest demand and accept limited service at times of greatest demand. Average rates paid per thousand cubic feet in 1953 were: (1) residential—72.9 cents; (2) commercial—55.7 cents; and (3) industrial—26.2 cents (Colby, et al., 1953).

**Gas Injection.** Natural gas is withdrawn from oil and gas fields of California in much larger amounts than the ordinary production figures indicate. For every 2 cubic feet of gas made available for consumption, nearly 1 cubic foot of gas is reinjected into oil-bearing and condensate-bearing formations for the purpose of increasing

Table 7. Fields employing gas injection in California in 1954.  
(Data from Conservation Committee of California Oil Producers.)

County	Field	Gas injected in 1954 (thousand cu. ft.)	Reason for injection
Fresno	Coalinga, East, Extension	6,990,005	PPM
Kern	Belridge, North	22,636,561	PPM
	Canal	2,221,379	PPM
	Coles Levee, North	27,470,836	PPM & PM
	Coles Levee, South	22,875,790	C—PPM
	Cymrie	866,201	PM
	Elk Hills	912,289	RP
	Greeley	5,249,032	PM
	McDonald Anticline	3,164	? Ex.
	Midway-Sunset (Buena Vista Hills area)	12,131,740	PPM & PM
	Paloma	34,314,360	C—PPM
	Rio Bravo	6,477,942	PPM
	Ten Section	704,062	RP—Ex.
Kings	Kettleman, North Dome	35,451,972	RP & PPM
Los Angeles	Castaic Junction	333,353	PPM
	Honor Rancho	766,928	PPM
	Newhall-Potrero	14,255,681	PPM
	Rosecrans	139,957	GS—Ex.
	Wilmington	2,771,104	RP & PPM
Orange	Coyote West	10,983,335	PPM
	Huntington Beach	514,933	GS & GS—Ex
Santa Barbara	Capitan	79,863	S—PM
	Cuyama, South	9,536,216	PPM
	Elwood	657,180	PM
	Lompoc	230,089	PPM
	Russel Ranch	7,166,784	PPM
State total		225,740,756	

C—Cycling  
S—Storage  
Ex—Experimental or pilot operation  
PM—Pressure maintenance  
PPM—Partial pressure maintenance  
RP—Repressure  
GS—Gas sweep

the recovery of liquid hydrocarbons. The injection methods used to obtain increased recovery may be considered to be of the following types (Uren, 1950, pp. 491-93): (1). Pressure maintenance—gas is injected into the oil reservoir before the field pressure has been appreciably reduced, with the purpose of maintaining or partially maintaining the field pressure as production proceeds. (2). Repressuring—gas is injected into the reservoir after the field pressure has declined to relatively low values, with the purpose of restoring or partially restoring the field pressure; meanwhile, all producing wells are temporarily shut in. (3). Gas sweep or drive—gas is injected into the oil-bearing formation for the purpose of creating a flow of gas through the reservoir rock from the injection wells to the producing wells. (4). Cycling—gas is injected under high pressure into the condensate reservoir for the purpose of forcing the condensate-bearing gas toward the producing wells and also to maintain a high reservoir pressure to prevent a retrograde condensation within the reservoir.

Each of the above methods of injection were employed in one or more California fields in 1954, with a total injection of 225,740,756 thousand cubic feet. Nearly all of this gas was treated at natural gasoline and cycle plants for removal of natural-gas liquids before being returned to the formations.





FIGURE 4. The Super Inch pipeline carrying natural gas from Texas and New Mexico spans the Colorado River on a steel arch bridge (at far left) near Needles, California. The Pacific Gas and Electric Company's compressor station across the river (upper middle) helps push the gas to central and northern California markets. Completion in 1957 of an adjacent pipeline bridge will help to fulfill California's future natural gas requirement. *Photo courtesy Pacific Gas and Electric Co.*



In addition to gas injected for purposes of increased production of liquid hydrocarbons, smaller amounts of gas are injected for storage or conservation purposes. Storage facilities are operated by utility companies at La Goleta, Newhall-Potrero, Playa del Rey, Whittier and other areas. This type of operation is an important part of the gas distribution system of California and in a sense is a conservation measure in the elimination of gas wastage during periods of low utilization and/or high oil production.

Table 8. California natural gas imports—1947-54.

(Conservation Committee of California Oil Producers, 1955, Table XXXI.)

Year	Imports (thousands of cu. ft.)	Year	Imports (thousands of cu. ft.)
1947.....	3,490,204	1951.....	243,749,325
1948.....	65,560,331	1952.....	297,678,553
1949.....	94,098,642	1953.....	357,118,918
1950.....	148,038,917	1954.....	465,550,711

**Imports.** Prior to 1947, California's natural gas requirements were supplied entirely from resources within the state. However, as discoveries of new sources of natural gas have not kept pace with rising demand, the importation from other states has become necessary. In 1947, a pipeline was completed by El Paso Natural Gas Company, which supplied California with 3,500,204 thousand cubic feet of gas that year. Since that time an enormous increase in the importation of natural gas has been necessitated by the rapid rise in population and industrialization, the increased use of local gas for repressuring oil fields, and the decreased supply and reserves. In 1954, the total gas imported into California was 465,550,711 thousand cubic feet, which was nearly equal to the state's total production and was an increase of 30 percent over the previous year.

Natural gas imported by California is piped from the Permian basin of west Texas and southeast New Mexico and from the San Juan basin of northwest New Mexico. Nearly half of this gas is supplied to the Pacific Gas and Electric Company at Topock, Arizona (near Needles, California) and the balance is delivered to the Southern California and Southern Counties Gas Companies at Ehrenberg (near Blythe, California) (Conservation Committee, 1955, p. 72).

The fast-growing population of California probably will require that natural gas be imported into the state at an increasing rate for at least the next few years. These added imports can be supplied by the Permian and San Juan basins in the near future, and possibly even by Canadian fields in the distant future. In order to handle the expected continuous import increases, El Paso Natural Gas Company and the three gas-importing companies of California are constantly planning and constructing new pipeline facilities.

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# NATURAL-GAS LIQUIDS

BY EARL W. HART

Natural-gas liquids rank second in value among the mineral commodities produced in California, just ahead of natural gas and exceeded only by petroleum. The production of natural-gas liquids from petroleum and gas wells in the state has increased for many years, although a slight decrease was noted in 1954. Partial figures indicate that the production for 1955 will be about the same as that of the preceding year (Knudsen, 1955). In recent years the production of natural-gas liquids in California has been restricted somewhat by the lack of important new discoveries of reserves. The known reserves have remained rather constant for the past decade, being 330,249,000 barrels on December 31, 1954. Although the trends in the uses of natural-gas liquids change almost continually, two definite trends seem to be indicated in 1955: (1) The petrochemical industry will continue to use more and more liquefied petroleum gases and natural gasoline products, as well as to develop new uses for these raw materials; and (2) the demand for higher octane gasoline will cause the refineries to reform natural gasoline catalytically, or process it some other way to increase the octane before blending with refinery gasoline.

**Definitions.** Natural-gas liquids are those liquid hydrocarbons that are obtained from natural gas by absorption and condensation. The principal liquids so obtained are grouped as natural gasoline, cycle condensate, and liquefied petroleum gases. The liquefied petroleum gases (LP-gases) are composed of propane, normal (n-) butane and isobutane, which are produced and utilized separately or as various mixtures. Liquefied refinery gases (LR-gases) are the same as LP-gases, except LR-gases are not obtained from natural gas by extraction, but rather are products of petroleum cracking and other refinery processes. LR-gas sales figures are included with LP-gas sales figures, but the production figures are separate.

**Occurrence and Composition.** Natural gas, from which natural-gas liquids are obtained, occurs in subsurface reservoirs. Within these reservoirs, the gas exists in three natural environments: (1) Dissolved in crude oil; (2) associated (in contact) with crude oil as a gas cap; and (3) not associated with crude oil. The reservoirs containing natural gas dissolved in or associated with crude oil yield all of the natural-gas liquids in California. Natural gas not associated with oil contains too small an amount of natural-gas liquids for these liquids to be commercially extracted in California.

Wells in the Los Angeles basin, southern San Joaquin Valley, and coastal region which includes Ventura, Santa Barbara, and San Luis Obispo Counties supply all of the natural-gas liquids produced in the state. The 10 fields that were most productive of such liquids in 1953 were, in order, (1) Ventura Avenue, (2) Kettleman Hills, (3) Paloma, (4) Long Beach, (5) Huntington Beach, (6) South Coles Levee, (7) Wilmington, (8) Richfield, (9) Santa Fe Springs, and (10) Midway-Sunset (from the U. S. Bureau of Mines, unpublished data).

The composition of natural gas in California, as elsewhere in the world, varies from field to field. The volatile portions are composed essentially of hydrocarbons of the paraffin (methane) series in which methane ( $\text{CH}_4$ ) is predominant, followed by decreasing proportions of ethane ( $\text{C}_2\text{H}_6$ ), propane ( $\text{C}_3\text{H}_8$ ), butanes ( $\text{C}_4\text{H}_{10}$ ), pentanes ( $\text{C}_5\text{H}_{12}$ ), and the heavier paraffin hydrocarbons. The principal gaseous impurities are nitrogen (N), carbon dioxide ( $\text{CO}_2$ ) and hydrogen sulfide ( $\text{H}_2\text{S}$ ). These impurities generally amount to a small percentage of the gas but may amount to 10 percent or considerably more.

Table 1. Physical properties of a few of the natural hydrocarbons of the paraffin (methane) series.

(After Interstate Oil Compact Commission, Oil and gas production, 1951, Table II, p. 26.)

Name	Chemical formula	Condition at 60° F. & 14.63 psi	Boiling pt. in °F. at normal conditions	Gas or liquid in which contained
Methane.....	$\text{CH}_4$	Gas	-258.5	Natural gas
Ethane.....	$\text{C}_2\text{H}_6$	"	-127.5	" "
Propane.....	$\text{C}_3\text{H}_8$	"	-43.9	LP-gases
N-Butane.....	$\text{C}_4\text{H}_{10}$	"	31.1	" "
Iso-Butane.....	$\text{C}_4\text{H}_{10}$	"	13.6	" "
N-Pentane.....	$\text{C}_5\text{H}_{12}$	Liquid	96.9	Natural gasoline or condensate
Iso-Pentane.....	$\text{C}_5\text{H}_{12}$	"	82.3	" " " " "
N-Hexane.....	$\text{C}_6\text{H}_{14}$	"	155.8	" " " " "
Iso-Hexane.....	$\text{C}_6\text{H}_{14}$	"	140.4	" " " " "
N-Heptane.....	$\text{C}_7\text{H}_{16}$	"	209.1	" " " " "
Iso-Heptane.....	$\text{C}_7\text{H}_{16}$	"	194.0	" " " " "
N-Octane.....	$\text{C}_8\text{H}_{18}$	"	258.2	" " " " "
Iso-Octane.....	$\text{C}_8\text{H}_{18}$	"	210.5	" " " " "
Other paraffins.	$\text{C}_n\text{H}_{2n+2}$	"	----	" " " " "

Natural gas is generally classified in the field as "dry" or "wet." Dry gas contains little or no liquid hydrocarbons and therefore is not processed for the natural-gas liquids. Wet gas contains varying amounts of the natural-gas liquids which can usually be extracted if enough natural gas is available. The normal products derived from wet gas are natural gasoline and the liquefied petroleum gases.

A special type of wet gas is condensate or retrograde gas which exists in the subsurface reservoir under very high pressures, usually more than 3500 pounds per square inch. This gas is similar to other wet gases, but it contains larger amounts of the heavier paraffins plus certain other hydrocarbons of kerosenes and naphthas. The products obtained from a condensate field are natural gasoline, LP-gases, and cycle (debutanized) condensate.

**Natural Gasoline and Cycle Plants.** The processing of wet gas to obtain the various natural-gas liquids is done at natural gasoline and cycle plants in or close to the producing fields. (For the locations of oil fields, in California, see the map in the petroleum section of this bulletin.) The principal type of gasoline plant used in California, and elsewhere, employs a combination compression-oil absorption process. In this process, the wet gas is first subjected to pressure and cooling, which con-



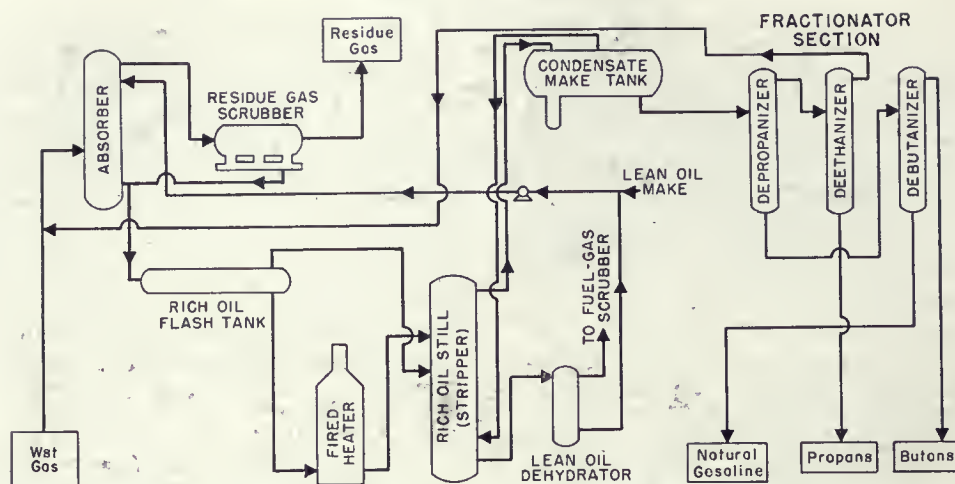


FIGURE 1. Simplified flow sheet of a typical natural gasoline plant using a compression-oil absorption process.

condenses out some of the liquids and removes any traces of crude oil. Then, the gas is bubbled through a special absorption oil, which has been cooled. This oil absorbs the volatile gas liquids, leaving the residue gas "dry." The "rich" oil is then heated and fed to a series of distillation towers. With the aid of heat and steam, the gas liquids are stripped from the absorption oil, which is returned for reuse. Then each of the gas liquids—natural gasoline, butane, and propane—is distilled out in fractionating towers at each one's particular temperature. Meanwhile, the dry residue gas may be sent to compressors for injection into the formation in order to repressure the reservoir or it may be sold as fuel. Some of the residue gas commonly is used to operate the gasoline plant (Standard Oil Co., 1955).

The cycle plants in California, at Paloma and South Coles Levee, are similar to gasoline plants in that they employ the compression-oil absorption method as part of the condensate gas processing. However, they have two additional features. (1) The wet gas from the conden-

Table 2. Largest capacity gasoline plants and cycle plants in California as of January 1, 1954.

(Data from Knudsen, 1954.)

Gasoline plants	Daily capacity in barrels		
	Natural gasoline	LP-gases	Total
Shell Oil Co. at Ventura.....	7,142	1,786	8,928
Standard Oil Co. at Kettleman Hills...	1,858	3,570	5,428
Tidewater Assoc. Oil Co. at Ventura... (plants 2, 4, and 6)	2,150	2,350	4,500
Richfield Oil Corp. at N. Coles Levee...	952	2,976	3,928
Wilmington Gasoline Co. at Wilmington...	1,667	1,515	3,182
P. S. Magruder at Kettleman Hills... (Western States plant)	1,667	1,428	3,095
Signal Oil and Gas Co. at Huntington Beach...	2,400	617	3,017
Lomita Gasoline Co. at Long Beach...	2,600	400	3,000
Cycle plants	Daily capacity in barrels		
	Natural gasoline & condensate	LP-gases	Total
Western Gulf Oil Co. at Paloma.....	5,200	3,500	8,700
Ohio Oil Co. at S. Coles Levee.....	3,400	1,500	4,900

Table 3. Production of natural-gas liquids in California—1953-54.  
(Data from U. S. Bureau of Mines.)

Year	Production (thousands of barrels)			
	Natural gasoline	LP-gases	Cycle condensate	Total natural-gas liquids
1954.....	19,007	9,620	2,094	30,721
1953.....	19,328	9,466	2,347	31,141

<sup>1</sup> Preliminary figure.

sate reservoir is initially processed by a series of heat exchangers and separators to remove the heavier fractions of the gas liquids, which results in the product known as cycle or debutanized condensate. The remaining wet gas is further processed by normal gasoline plant methods. (2) The residue gas, from which the liquid fraction has been removed, is compressed to a high pressure (4000 pounds per square inch or more) and injected into the formation in order to force the condensate-bearing gas in the reservoir to the producing wells to allow for a high recovery of the natural-gas liquids.

On January 1, 1954, seventy-one natural gasoline and two cycle plants operated in California with a total daily capacity of 75,460 barrels of natural gasoline and cycle condensate and 36,410 barrels of liquefied petroleum gases (Knudsen, 1954). This ranked California second behind Texas, with 14 percent of the total plants and 12 percent of the total capacity in the country. The capacity of California natural-gasoline plants was down slightly from January 1, 1953. The number of plants in California has decreased sharply from a maximum of 172 in 1926 (API, 1929, p. 153), and since that time there has been a clear trend toward fewer plants with larger capacities. However, a leveling-off was reached in 1947-48, after which there was only a slight decrease in the number and an increase in the total capacity of the plants (API, 1950, pp. 204-205).

New gasoline plants were built at South Cuyama in 1950, Belgian anticline in 1952 and Castaic in 1954. During the same period five plants were shut down or dismantled at Brea-Olinda, Rosecrans, Montebello,





FIGURE 2. Natural gasoline plant at Elk Hills field in Kern County. Photo shows absorption, distillation, and fractionating towers at right, cooling tower in center, furnaces in background and storage tank at far left. Photo courtesy of Standard Oil Company of California.

Midway-Sunset and Signal Hill (Long Beach). Unfortunately, the Arvin-Tehachapi earthquake of July 21, 1952, caused severe damage to the cycle plant at Paloma, 16 miles southeast of Bakersfield and resulted in an explosion and fire. The damage was estimated at \$1,800,000 and about 4½ months of repair work was required to get the plant back to normal production (Johnston, 1955).

The distribution, by companies and number of plants, of the operating natural-gasoline and cycle plants in California on January 1, 1954, were:

Standard Oil Co. of California	16
Union Oil Co. of California	12
Shell Oil Co., Inc.	7
General Petroleum Corp.	4
Richfield Oil Corp.	3
Signal Oil and Gas Co.	3
The Texas Co.	3
21 other operators of one or two plants each	25
Total	73

**Production.** Production of natural gasoline was first recorded in California about 1911 and production of liquefied petroleum gases began about 15 years later. The Paloma field accounted for the first cycle-condensate production in 1944. The production of natural gas-liquids rose steadily at first, increased rapidly from 1923 to 1929, dropped during the depression years, and began to rise again in 1935. Beginning in 1943 another strong trend upward was initiated, culminating in a peak production in 1953 of 31,141,000 barrels of natural-gas liquids which was valued at \$107,652,000. In that year, California produced 13 percent of the national total, and was exceeded only by Texas, which produced more than half the national total. California recorded a slight decrease in production in 1954.

More than 570 billion cubic feet of natural gas was processed in California in 1954, from which 30,721,000<sup>1</sup> barrels of liquids were produced. The average yield of

Table 4. Production of natural-gas liquids in California.\*  
(Thousands of barrels.)

Year	Production	Year	Production
1911	5	1934	12,086
1912	25	1935	12,962
1913	83	1936	14,569
1914	185	1937	15,274
1915	306	1938	16,438
1916	409	1939	15,251
1917	686	1940	15,122
1918	768	1941	15,709
1919	932	1942	15,079
1920	1,148	1943	16,508
1921	1,386	1944	18,364
1922	1,598	1945	21,232
1923	4,127	1946	21,679
1924	5,537	1947	25,336
1925	7,219	1948	26,549
1926	9,271	1949	27,154
1927	11,858	1950	28,328
1928	13,907	1951	29,533
1929	20,008	1952	30,114
1930	19,755	1953	31,141
1931	16,199	1954	30,721
1932	13,128		
1933	11,904	Cumulative total	579,623

\* Statistical sources by years: 1911-31, U. S. Bur. Mines; 1932-40, Petroleum World; 1941-45, Am. Petroleum Inst. and U. S. Bur. Mines; 1936-54, U. S. Bur. Mines.

<sup>1</sup> Preliminary figure.

natural gas treated at natural-gasoline and cycle plants amounted to .0537 barrels or 2.25 gallons<sup>2</sup> per 1,000 cubic feet. The average yield has been relatively constant for the last several years.

**Reserves.** Texas has 56 percent of the natural-gas liquid reserves in the United States, followed in turn by Louisiana (17 percent), New Mexico (6 percent), Oklahoma (6 percent), and California (6 percent). California reserves have increased very little since 1946, amounting to 330,249,000 barrels on December 31, 1954. Of the state's total reserves, 68 percent is dissolved in crude oil and 32 percent is associated with crude oil as a gas cap (Am. Gas Assoc., 1955, p. 11).

<sup>2</sup> One barrel equals 42 U. S. gallons.

<sup>1</sup> Preliminary figure. A later preliminary figure of the U. S. Bureau of Mines indicates total production to be 30,411,000 barrels valued at \$104,673,000.



Table 5. Production of natural-gas liquids in California by month and type of liquid for 1954.\*

Month	Gas treated (million cu. ft)	Production in thousands of barrels						
		Natural gasoline	Butane-propane mixtures	Other LPG mixtures	Propane	Butanes	Iso-butane	Debutanized condensate
January	48,890	1,566	99	84	589	115	73	181
February	45,265	1,385	102	68	476	115	77	164
March	48,779	1,558	120	83	476	110	99	182
April	47,924	1,516	120	74	407	126	83	176
May	49,238	1,652	109	78	283	115	95	180
June	47,835	1,618	96	67	295	138	79	167
July	48,625	1,714	90	80	280	135	78	171
August	46,310	1,691	95	73	290	133	71	181
September	47,028	1,622	98	74	325	114	79	173
October	47,704	1,633	111	73	445	120	81	173
November	46,600	1,529	105	72	533	117	77	169
December	48,474	1,523	96	73	644	137	69	174
Total	572,672	19,007	1,241	899	5,043	1,475	961	12,094

NOTE: The production of propane is sharply reduced from May through September. This is a reflection of the decreased demand for propane as a fuel for heating purposes during the summer.

\* Preliminary figures obtained from U. S. Bur. Mines monthly *Petroleum Situation in District Five*, by Koudsen, E. T., Jan.-Dec. 1954.

<sup>1</sup> Adjusted figure.

Table 6. Production of natural gasoline and liquefied petroleum gases by counties—1953.

(Data supplied by U. S. Bur. Mines.)

County	Natural gasoline		Liquefied petroleum gases	
	Barrels	Value	Barrels	Value
Fresno <sup>1</sup>	1,387,000	\$5,940,000	1,293,000	\$3,284,000
Kern	25,659,000	\$22,261,000	2,850,000	7,213,000
Kings <sup>1</sup>	630,000	2,460,000	821,000	1,913,000
Los Angeles	6,377,000	25,485,000	1,084,000	2,175,000
Orange	3,090,000	12,818,000	1,182,000	2,604,000
San Luis Obispo	166,000	699,000	277,000	599,000
Santa Barbara	1,003,000	3,858,000	525,000	1,025,000
Ventura	3,363,000	12,170,000	1,434,000	3,148,000
Total	21,675,000	\$85,691,000	9,466,000	\$21,961,000

<sup>1</sup> Natural-gas liquids processed in Kettleman Hills oil field came from gas produced in both Kings and Fresno Counties. Such production is here entirely assigned to Kings County, where the processing plants are located.

<sup>2</sup> Includes cycle condensate.

Table 8. Distribution of natural-gas liquids produced in California in 1954.

(Data from U. S. Bur. Mines.)

Natural-gas liquids	Pro-duction	Shipments			
		Within Calif., Ore., Wash., Nev., & Ariz.,		To pts. outside Calif., Ore., Wash., Nev., & Ariz.	Total
		To refin-eries	Other uses		
LP-gases	9,620	5,091	4,463	139	9,693
Natural gasoline	19,007	18,650	28	323	19,001
Cycle condensate	2,094	1,679	0	396	2,075
Total	30,721	25,420	4,491	858	30,769
Percentage of total shipments		82.6	14.6	2.8	100.0

Table 7. Estimated proved recoverable reserves of natural-gas liquids in California on December 31 for the years 1946-54<sup>1</sup> (Thousands of barrels.)

	1946	1947	1948	1949	1950	1951	1952	1953	1954
Non-associated	40,328	36,900	--	--	--	--	--	--	--
Associated	107,300	115,605	103,259	108,564	137,492	112,854	108,720	105,936	104,137
Dissolved	160,644	159,646	204,659	211,711	225,895	216,462	213,787	218,930	226,112
Total	308,272	312,151	307,908	320,275	363,387	329,316	322,507	324,866	330,249
% of U. S. total	10%	10%	9%	9%	9%	7%	6%	6%	6%

<sup>1</sup> Estimated by Am. Gas Assoc. and Am. Petroleum Inst.

**Distribution.** Of the natural-gas liquids produced in 1954 in California, 82.6 percent was shipped to refineries in California, Oregon, Washington, Nevada, and Arizona, 14.6 percent was sold for use as a fuel and in the chemical and synthetic rubber industries in the same states, and 2.8 percent was shipped outside of these states.

**Utilization.** Nearly all of the natural gasoline and cycle condensate produced in California goes to the refineries, mostly to be used in the manufacture of

automotive fuels. The blending of natural gasoline with refinery gasoline has been an accepted practice. However, the demand for higher octane gasolines has been increasing and the light paraffins of natural gasoline do not lend themselves well to this purpose. Therefore, the pentanes are often removed for non-gasoline uses, then the natural gasoline is catalytically reformed to produce cyclic and aromatic fractions which are blended with refinery gasoline to improve the octane ratings (Crockett, 1955). Under some conditions of extraction,





FIGURE 3. Large LP-gas hand burner used to control weed growth in irrigation ditches and alongside roads. Weeds are killed by passing high temperature flame over them at a rate of about  $1\frac{1}{2}$  miles per hour. After sun dries weeds, a fast second pass clears ditch or roadside of all debris. A 250-gallon trailer-mounted gas tank supplies fuel which is used at a rate of about 15 gallons per hour. *Photo courtesy LP Gas Association.*



Table 9. Sales of LP-gases and LR-gases in California in thousands of barrels—1953-54.

(After Coumbe and Avery, 1954.)

Uses	Butane		Propane		Mixture		Totals	
	1953	1954	1953	1954	1953	1954	1953	1954
Domestic and commercial.....	0	0	2,366	2,731	1,755	1,234	4,121	3,965
Gas manufacturing.....	0	0	100	128	10	11	110	139
Industrial.....	0	0	146	105	18	26	164	131
Synthetic rubber.....	883	259	1	165	0	16	884	440
Chemical plants.....	397	772	730	821	0	1	1,127	1,594
Internal combustion.....	0	0	851	675	700	512	1,551	1,187
All other.....	19	0	19	57	16	0	54	57
Total.....	1,299	1,031	4,213	4,682	2,499	1,800	8,011	7,513

cyclohexane, benzene, toluene, and the xylenes, among other products, are produced to be used in aviation gasoline, as solvents, and in the manufacture of petrochemicals (explosives, plastics; dyes, insecticides, pharmaceuticals, etc.).

The uses of LP-gases are as varied as those of natural gasoline. More than half of the LP-gases produced are shipped to the refinery. Here the butanes are important since they are required for use in improving the volatility of gasoline. The LP-gases not shipped to refineries are sold, along with LR-gases for domestic and industrial uses. These uses and the percentages of total LP-gases sold in California in 1954 are: (1) domestic and commercial heating—53 percent; (2) chemical (petrochemical) plants—21 percent; (3) internal combustion in tractors, buses, etc.—16 percent; (4) synthetic rubber industry—6 percent; (5) gas manufacturing—2 percent; (6) industrial fuel and other uses—2 percent (Coumbe, 1954).

Compared with 1953, the 1954 LP-gas sales dropped more than 5 percent. Decreased demand for synthetic rubber accounts for part of the drop, and sales for internal combustion were also substantially reduced. Contrary to the overall decrease, a 40 percent increase in sales to chemical plants was registered in 1954, and a strong trend toward continued expansion of the petrochemical industry is indicated.

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## NICKEL

By SALEM J. RICE

More than 60 percent of the free world's output of nickel is consumed in the United States, but domestic sources account for less than 1 percent of the total virgin nickel production. This deficiency is especially critical because most of the new supply of the metal has been diverted to defense purposes in recent years, thus creating a serious shortage for civilian manufacture. By the diverse uses of its many alloys, nickel finds its way into almost every phase of American domestic and industrial life, from kitchen utensils and appliances to experimental jet and rocket research. Many attempts have been made by the government to stimulate production, both domestic and foreign, but in 1956 the demand for nickel apparently still considerably exceeded the supply.

Canada is the principal source of nickel, accounting for about 85 percent of the free world production. Other significant sources are New Caledonia, Cuba, and Norway.

Although California has no recorded nickel production, evidence of several types of nickel mineralization are widespread in the state and the possibility of commercial production appears reasonably good.

### Mineralogy and Geologic Occurrences

Nickel, a silvery white metal, ranks twenty-fourth in abundance among the elements of the earth's crust. For example, it is a more abundant metal than copper, lead, and cobalt, but less abundant than zinc, chromium, and manganese.

Although nickel occurs as a major constituent of numerous minerals, only a few of these are of commercial significance as ore minerals. It has not been found as the pure native metal, but it is alloyed with iron in some meteorites and in a few rare terrestrial minerals. Most of the nickel minerals are sulfides, arsenides, or hydrated silicates. The principal ore minerals are the sulfides pentlandite ( $(\text{Ni}, \text{Fe})\text{S}$ ), polydymite ( $\text{Ni}_3\text{S}_4$ ), and millerite ( $\text{NiS}$ ); the arsenides niccolite ( $\text{NiAs}$ ) and chloanthite ( $\text{NiAs}_2$ ); and garnierite, a hydrated silicate of nickel and magnesium. Of these, pentlandite and garnierite are by far the most important. Pentlandite has a metallic luster and a light bronze-yellow color. It varies considerably in its nickel content, the iron and nickel being mutually replaceable. Garnierite is a soft, green claylike mineral containing variable amounts of nickel and magnesium. Its color ranges from pale green in low-nickel varieties to deep bluish green in high-nickel varieties (Pecora, Hobbs, and Murata, 1949).

Nickel can substitute for magnesium and ferrous iron in most crystal structures, and it is thus found in numerous places as a minor constituent of minerals not ordinarily considered to be nickeliferous. In places such minerals are sufficiently enriched and abundant to constitute nickel ores. One of the most important of these is pyrrhotite, an iron sulfide. Magnesium-rich minerals such as olivine and serpentine commonly contain small amounts of nickel where they are constituents of basic and ultrabasic igneous rocks. For example, most intrusive serpentine contains 0.1 to 0.3 percent nickel, and in places the percentage is raised to as much as 2 percent

by supergene enrichment involving replacement of magnesium by nickel.

Nickel is most easily detected in rocks and minerals by dissolving the material with acids, neutralizing with ammonium hydroxide, and adding dimethylglyoxime to the filtered solution. If nickel is present, a scarlet precipitate of nickel-dimethylglyoxime is formed. This is a very sensitive test. Nickel sulfides can be detected simply by licking the specimen and rubbing dimethylglyoxime powder on the test area. The presence of nickel sulfide grains is indicated by scarlet spots.

The important ores of nickel are of two distinct types, which differ widely in occurrence and in mode of origin. These are (1) the primary ores, comprising the nickel-bearing sulfides and arsenides, and occurring as magmatic segregations or in veins deposited at considerable depths by rising solutions; and (2) the secondary or lateritic ores, largely nickel silicates and oxides, which were enriched by descending solutions and concentrated at or near the surface by weathering processes.

*Nickel Sulfide Ores.* Most of the world nickel production is obtained from complex primary ores that contain sulfides of nickel and copper. These ores consist principally of pyrrhotite, and also contain subordinate pentlandite and chalcopyrite. Minor percentages of gold, silver, platinum, cobalt, selenium, and tellurium are also commonly present, and in many places one or more of these are recovered in addition to nickel and copper.

All of the principal nickel sulfide deposits are closely associated with basic or ultrabasic igneous rocks such as gabbro and peridotite. In these deposits the sulfides occur principally as magmatic segregations, or as replacement masses or veins within or adjoining the igneous rocks. The deposits near Sudbury, Ontario, which have yielded more than 80 percent of the total world nickel production since 1905, are localized at or near the base of a huge sill-like intrusion of norite, a variety of gabbro.

The Sudbury norite body crops out in a great ellipse 36 miles long and 17 miles wide. It is presumed to be spoon-shaped, being buried in the central portion of the basin beneath a thick cover of volcanic and sedimentary rocks. Large ore bodies have been found at about 15 localities along the lower contact of the norite and along a few faults below this contact. The nickel-bearing ore occurs as lenses of nearly pure sulfides, as stringers, as veins along shears, as disseminations, and as matrix in breccia. The ore mined at most of the deposits contains 0.8 percent to about 2 percent nickel, and similar amounts of copper. The average contains about 1.5 percent of each (Material Survey on Nickel, 1952, p. V-13). Most of the ore bodies are roughly tabular and steeply dipping. For example, the Falconbridge ore body is a continuous sheet of sulfides about 3,500 feet long that lies between the norite and the underlying greenstone. It dips almost vertically and ranges in thickness from a few inches to more than 100 feet, averaging approximately 15 feet. This ore body is being mined at a depth of about 4,000 feet and diamond drilling has shown that



it extends at least 5,600 feet below the surface (Loch-head, 1955).

Nickel sulfide deposits similar to those near Sudbury, but not as large, occur in South Africa, Russia, Europe, Alaska, and the United States.

*Lateritic Nickel Ores.* Lateritic nickel ores differ from the sulfide ores in both character and origin. They occur as blanket deposits on or near the surface, and the ore minerals are silicates and oxides. They originated by supergene enrichment resulting from intense chemical weathering of ultrabasic rocks, such as peridotite and serpentine, that normally contain small amounts of nickel.

Peridotite is a medium- to coarse-grained igneous rock composed principally of olivine and magnesium-rich pyroxenes. It is generally partly or completely altered to serpentine. Peridotite and serpentine derived from peridotite have unusual chemical compositions as compared with the bulk of the igneous rocks of the earth's crust. They are comparatively rich in magnesium and iron and low in silica, but contain only small percentages or traces of aluminum, calcium, potassium, and sodium, which are relatively abundant in most other igneous rocks. However, they are relatively rich in chromium, nickel, and cobalt. The nickel content of these rocks ordinarily lies between 0.1 and 0.3 percent, but such concentrations are at present too low for commercial exploitation.

Compared with most silicate minerals, olivine and the serpentine minerals are rather easily decomposed by acid solutions, even by the weak carbonic and other organic acids present in rain water and ground water. Thus under proper conditions of intense weathering, such as prevail in a humid tropical climate, peridotite and serpentine are decomposed to yield a thick soil mantle known as laterite. The magnesium and silica are leached from the surface zone, leaving a residual soil composed principally of relatively insoluble hydrous iron oxides. Most of the magnesium is carried away in solution, but in places much of the silica is deposited as opal, chalcedony, or quartz in joint cracks and other fractures in the underlying bedrock. After further disintegration of the interstitial bedrock the stockwork veins of quartz and chalcedony thus formed remain as a residual silica boxwork structure in the soil. The nickel, not being as soluble as magnesium, in part remains in the soil as a residual enrichment and in part is transported downward in solution to be deposited in the bedrock underlying the soil. The chromium and cobalt are concentrated in the soil.

Laterite forms only on areas of moderate relief where weathering proceeds more rapidly than erosion. In lateritic areas that have been subsequently eroded, the laterite is characteristically found only on relatively flat or gently sloping benches, terraces, ridge crests, and plateaus.

The exact composition and thickness of the nickeliferous laterite blanket varies from place to place, according to differences in such factors as climate, topography, and permeability of the bedrock. The soil, or laterite proper, is everywhere brick-red to ochre-colored and is composed principally of powdery and concretionary hematite and limonite. No distinct nickel minerals have been recognized in this material, but it gener-

ally contains 0.5 percent to 1.0 percent or more of nickel. In places this iron-rich soil grades downward to a zone of silica boxwork, which may be rich enough in garnierite to constitute relatively high-grade nickel ore. In general, garnierite is abundant only in association with silica boxwork, and selected ore from this zone commonly contains 5 percent or more of nickel. However, the silica zone may be absent or may consist of rather massive brown chalcedony which contains little nickel. Below the silica zone lie a few feet of moderately decomposed bedrock grading downward to fresh bedrock, into which sparse veins of garnierite and silica minerals penetrate along joint fractures. The highest grade of nickel ores normally occurs in the silica boxwork, where present, and in the partially decomposed bedrock at the roots of the laterite.

Garnierite-rich deposits are commonly referred to as nickel silicate ores. They are widely distributed in the world, notably in New Caledonia, Indonesia, Brazil, and at Nickel Mountain, Oregon. New Caledonia is second in importance only to Sudbury among the nickel-producing districts of the world, having been the principal source of nickel until 1905. About one-third of the island is underlain by peridotite and serpentine; much of it covered by a blanket of laterite which ranges in thickness from a few feet to more than 100 feet. Garnierite, the principal ore mineral, is concentrated in the silica zone beneath a thick surface zone composed principally of iron oxides. The commercial concentrations of garnierite are found only over fresh peridotite (de Chetelat, 1947). Extensive plateau areas underlain by peridotite have thick lateritic mantles containing approximately 2 percent nickel in their lower parts, and in some areas the ore averages 3 to 5 percent nickel.

The laterite deposit at Nickel Mountain, near Riddle, Oregon, is at present the most important domestic source of nickel. It is similar to the deposits in New Caledonia in that the laterite lies on fresh peridotite and the nickel occurs principally in garnierite which is concentrated in and just below the zone of silica boxwork (figure 1). At Nickel Mountain the lateritic blanket, ranging in thickness from a few feet to more than 60 feet, rests on a remnant of an old dissected erosion surface, known as the Klamath peneplain. The richest ore, containing an average of about 1.5 percent nickel, is found principally on broad benches in the crest area of the mountain. Terraces below 2,000 feet in elevation are apparently Pleistocene in age and are not mantled with laterite, indicating an earlier period of ore formation (Pecora and Hobbs, 1942).

Nickeliferous laterites that lack the silica boxwork zone and consist essentially of iron-rich soil are usually referred to as nickeliferous iron ores. Although they are relatively low in nickel content, deposits of nickeliferous iron ore are commonly measurable in hundreds of millions of tons, and constitute the bulk of the world's potential nickel reserves. The only deposit of this type of laterite presently being mined is at Nicaro, Cuba (De Vletter, 1955; Lutjen, 1954), although large deposits are known elsewhere in Cuba (McMillan and Davis, 1955) and in the Philippines, Celebes, and Borneo.

The laterite in Cuba is a deep, iron-rich soil derived from serpentinized peridotite. The top 3 to 6 feet is reddish-brown and consists of birdshot-size iron oxide



## IRON OXIDE-RICH SOIL

Upper few feet is brick red soil containing shot size iron oxide concretions. Grades down to soft ocher-yellow limonite. Brown hematite concretions or "pellets," and scattered residual "boulders" on surface.

## SILICA BOXWORK ZONE

Peridotite altered to soft ocher-yellow limonite. Former joint cracks filled with stockwork veins of silico minerals and garnierite. Scattered residual "boulders" of fresh peridotite.

## ROOT ZONE

Roots or ribs of boxwork project down into fresh peridotite along joint cracks.

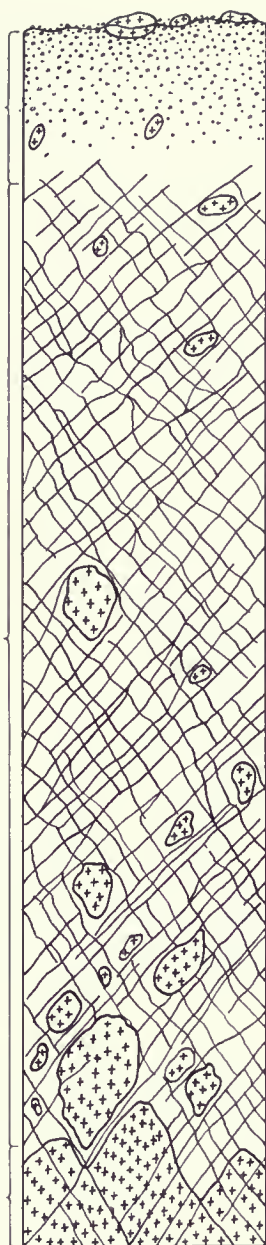


FIGURE 1. Diagrammatic sketch of vertical section of lateritic nickel deposit at Nickel Mountain, Oregon. Modified after Pecora and Hobbs, 1942, p. 215.

concretions in a powdery hematite-rich matrix. Below this the soil is ocher-yellow and composed principally of limonite. The soil contains scattered residual boulders of serpentine too massive to have been completely decomposed during lateritization. The nickel content of the soil increases downward from about 0.8 percent at the surface to about 1.6 percent at the base, although no specific nickel minerals have been recognized in this material. Below the soil in the area being mined is a zone of partly decomposed, nickel-enriched serpentine, which grades downward within a few feet into fresh serpentine. The enriched serpentine contains an average of about 1.6 percent nickel, whereas the fresh serpentine contains about 0.2 percent nickel. Although sparse vein-

lets of garnierite have been found in this zone, enrichment has apparently taken place principally by supergene replacement by nickel of some of the magnesium in the partially decomposed serpentine.

The total depth of the laterite blanket in Cuba ranges from a few feet to about 80 feet, but averages about 15 feet in the area being mined. The material mined and treated, including laterite and nickel-enriched serpentine, contains an average of about 1.4 percent nickel.

## Localities in California

Although there has been no recorded production of nickel from California, periodic interest has been indicated for many years by limited exploration of a few sulfide prospects. The recent discovery of potential deposits of nickeliferous laterite in the state, combined with the critical shortage of nickel, has resulted in renewed interest since 1954.

*Nickel Sulfide Ores.* Possibly the earliest serious efforts to develop a nickel prospect in California were made in the early 1900's at the Friday deposit in the Julian-Cuyamaca area of San Diego County. The geologic setting and mineralogy at the Friday mine are similar to those of many other nickel sulfide deposits in the world. The nickeliferous material, consisting principally of pyrrhotite with subordinate amounts of pentlandite and chalcopyrite, occurs in the Cuyamaca gabbro. The mineralized zone is an irregular body striking about N. 75° E. and dipping steeply northward. It was formed by replacement of the gabbro along fractures on the north side of an inclusion of schist that nearly parallels the ore in strike but dips about 60° southward. The surface outcrop of the Friday ore body is almost completely oxidized to gossan. Development work consists of a 160-foot vertical shaft with an incline extending to the 180-foot level, and drifts and crosscuts driven at the 132-foot and 180-foot levels. Partly oxidized sulfides are exposed at the 132-foot level and more massive sulfides on the 180-foot level, the lowest in the mine. Where exposed, the mineralized zone is from 6 feet to over 20 feet wide and 55 feet long; but its depth has not been fully determined. Assuming an average width of 15 feet and a length of 55 feet, there is estimated to be approximately 5,000 tons of indicated ore in a block between the 132- and 180-foot levels of the Friday shaft. Below the 180-foot level the mineralized body contains about 90 tons of inferred ore per foot of depth for a limited distance. The ore body probably averages from 2.5 percent to 3.0 percent nickel, the actual grade depending on the extent and degree of oxidation in the mineralized zone. In addition the ore is estimated to contain 0.5 percent to 1.0 percent copper, and as much as 0.15 percent cobalt is present (Creasey, 1946).

Elsewhere in the Julian-Cuyamaca area unexplored outcrops of gossan contain small amounts of nickel, and these suggest the presence of other nickel sulfide ore bodies (Creasey, 1946, p. 27).

In places the ultrabasic rocks of California (figure 2) contain an unidentified nickel-iron sulfide which is characteristically finely disseminated in the host rocks. The nickel-bearing mineral is gray, has a metallic luster, and is magnetic, the last property not characteristic of



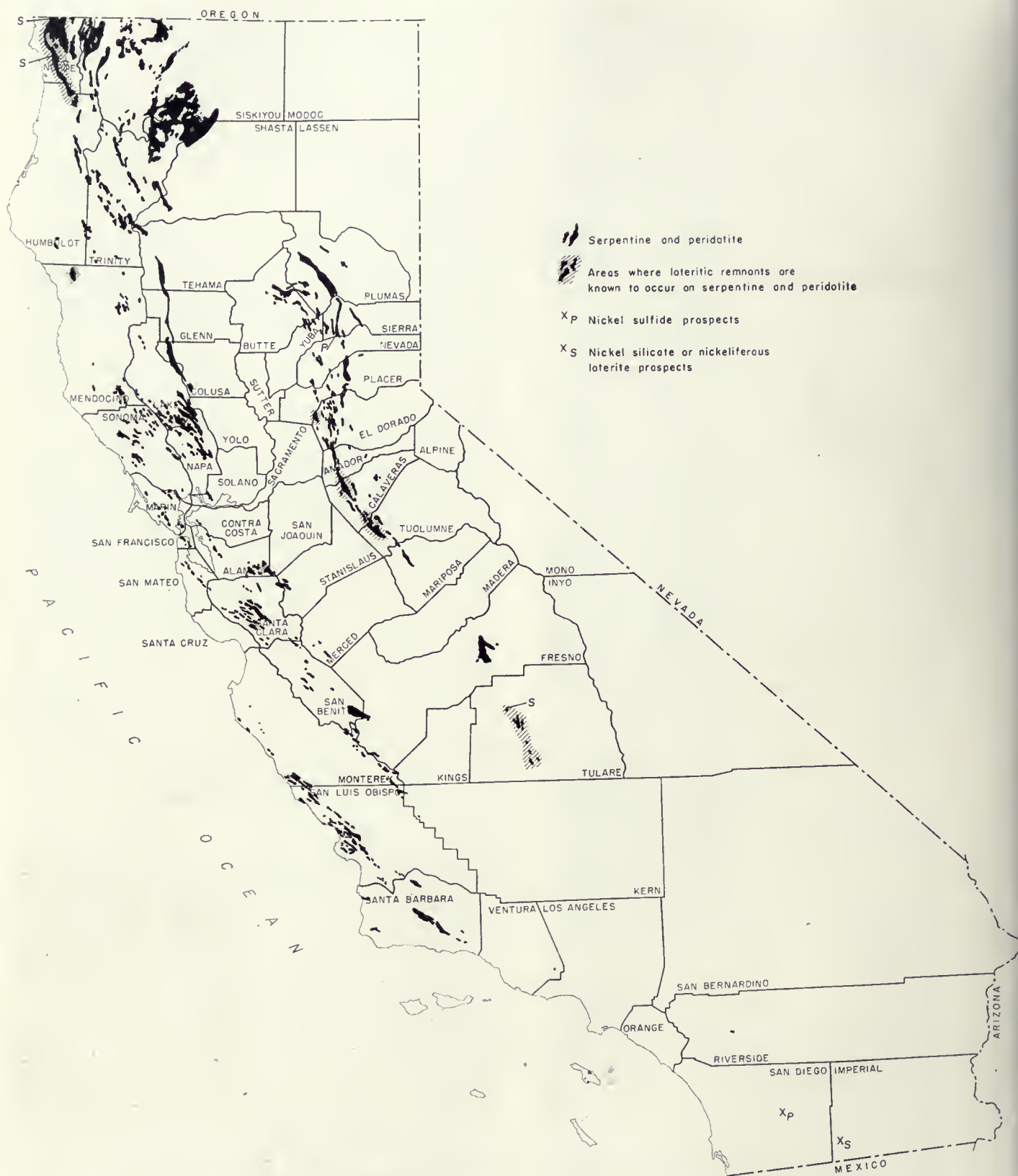


FIGURE 2. Map of California showing outcrops of ultrabasic rocks, areas known to contain lateritic remnants on these rocks, and locations of nickel prospects.





FIGURE 3. Northwestern portion of the Gasquet quadrangle, Del Norte County, California. Note low relief of crest areas of Pine Flat, High Plateau, Gasquet, and Cold Spring mountains. These are remnants of the Klamath peneplain, an Early Tertiary erosion surface. Almost all of the area included in this map is underlain by ultrabasic rocks. Nickeliferous laterite remnants occur only on the relatively flat crests and on benches and spurs down to an elevation of about 1800 feet.

most or all described nickel sulfides. It has not been previously described from California, but during 1956 three separate occurrences were called to the attention of the Division of Mines. Two of these were in serpentine, one from the Alleghany district of Sierra County and the other from Red Mountain in Del Norte County, while the third was in talc schist in the Colfax area of Placer County. These discoveries have not been evaluated, and may be quite local, but they are considered significant because of the large amount of ultrabasic rock in California.

**Nickeliferous Laterite.** Although the lateritic nickel ores at Nickel Mountain, Oregon, were discovered about 75 years ago, the presence of nickeliferous laterite in California was recognized only in the early 1950's. Like the Oregon occurrences, laterite in California has been found only on remnants of old erosion surfaces.

In the northwestern part of the state, nickeliferous laterite occurs on remnants of an early Tertiary erosion surface of low relief, known as the Klamath peneplain (Diller, 1902), that once extended over much of the Klamath Mountains area. Although extensively dissected by later streams, remnants of this surface have been preserved as relatively flat-topped mountains and ridges (figure 3). The largest remnants are found in Del Norte and northern Humboldt Counties, for intensive glacial and stream erosion during Pleistocene time largely destroyed it in the central and eastern parts of the Klamath Mountains.

The principal localities in northwestern California where nickeliferous laterite has been found to date are on the flat crests and slightly lower benches, shoulders, and saddles, of Pine Flat, High Plateau, Low Plateau, High Divide, Gasquet, Elk Camp, Little Rattlesnake, Rattlesnake, and Red Mountains, all in Del Norte County. All of the mountains listed above are underlain by peridotite or serpentine. Areas of laterite are indicated by deep brick-red soil rich in brown hematite concretions. Scattered residual boulders of the bedrock are commonly strewn on the surface, and in places leached fragments of quartz boxwork are abundant (figure 4). At a depth of 2 or 3 feet the pisolitic brick-red soil grades into light, friable ocher-yellow soil. Garnierite-rich boxwork, which constitutes the richest ore at Nickel Mountain, Oregon, is not exposed in any of the localities examined. Grab samples of surface soil collected by the Division of Mines from Pine Flat, Rattlesnake, and Red Mountain contained 0.56 to 1.02 percent nickel, whereas auger samples of ocher-yellow soil at depths of 9 to 11 feet contained 0.83 to 1.16 percent nickel. No specific nickel minerals were detected in the samples analyzed. The only exploration work done in this area by the latter part of 1956 consisted of trenches 5 to 10 feet deep at the Pine Flat Mountain and Little Rattlesnake Mountain deposits.

The region presently occupied by the Sierra Nevada also was occupied by an erosion surface of low relief



FIGURE 4. Typical silica boxwork from nickeliferous laterite. Exposed by bulldozer at Elk Camp Ridge, Del Norte County.



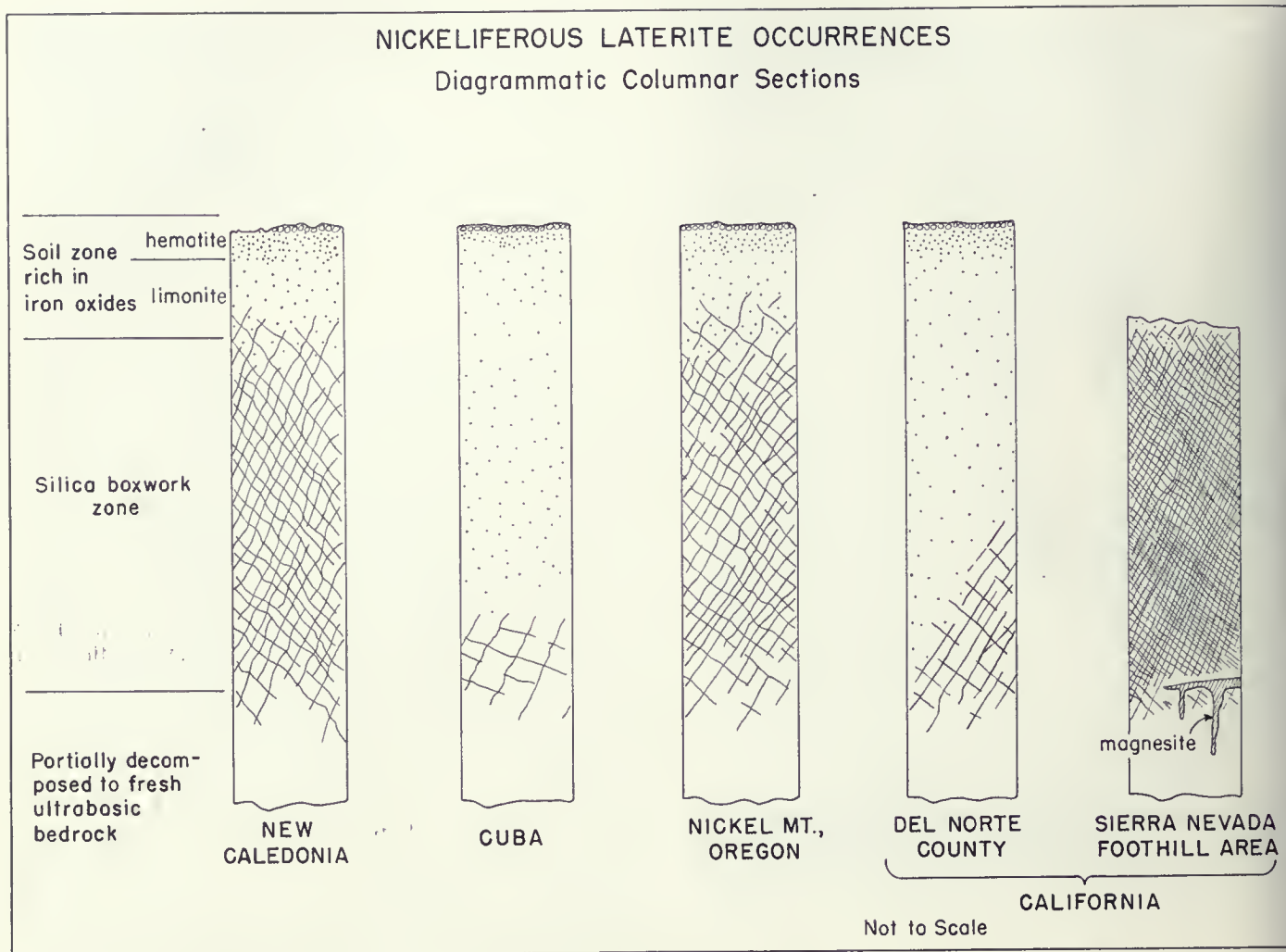


FIGURE 5. Comparative vertical sections of nickeliferous laterite from various localities.

during early Tertiary time, and was subjected to lateritic weathering. Remnants of this surface may be recognized as relatively flat to low rolling uplands forming interstream divides in the foothill belt, the late Tertiary and Quaternary streams generally having cut well below the old levels. The lateritic remnants on serpentine in this province largely consist of resistant cappings of rather dense silica boxwork grading into jasperlike silicified serpentine (Rice and Cleveland, 1955). In places these cappings are more than 100 feet thick. Garnierite occurs in places as cavity fillings in the silica boxwork and as veins in the silicified serpentine and fresh serpentine below it, but in areas examined the rocks are rather thoroughly leached and the average nickel content is less than 0.5 percent.

These siliceous lateritic remnants are well exposed in the area of the Pilliken chromite mine in El Dorado County, a few miles east of Valley Springs in Calaveras County, and in the Venice Hills and Deer Creek areas of Tulare County. The only exploration through 1956 was done in a small area in the eastern part of the Venice Hills, Tulare County, where previous excavations for chrysoprase had exposed veins of garnierite in silicified serpentine. Figure 5 diagrammatically com-

pares vertical sections of nickeliferous laterite occurrences in California with those from other well known areas.

In the Coyote Mountains of western Imperial County, supergene nickel enrichment in the weathered zone of a mass of pyroxenite has stimulated sporadic prospecting since about 1915. Small amounts of secondary copper minerals are present in addition to traces of garnierite in the partially decomposed rock. Development work is limited to few shallow excavations in the weathered zone.

Nickel is one of the strategic mineral commodities for which exploration loans may be obtained from the U. S. Defense Minerals Exploration Administration. After a nickel prospect has been approved for such a loan, this agency will pay 75 percent of the cost of recommended exploration.

#### Utilization

The greatest value of nickel lies in the qualities it imparts to its various alloys. When properly combined with other metals, it profoundly affects the strength, ductility, toughness, electrical resistance, coefficient of expansion, strength at high temperatures, resistance to corrosion, and magnetic properties of the resulting



alloys (National Bureau of Standards, 1948; Materials Survey—Nickel, 1954).

Approximately 20 to 25 percent of the nickel consumed in the United States is used in the production of stainless steels. These steels, known as the 300 series, contain chromium and nickel alloyed with iron. Type 302, containing 18 percent chromium and 8 percent nickel, accounts for about two-thirds of stainless steel production. Other types in the 300 series contain different proportions of these metals or small amounts of other constituents, such as silicon, carbon, columbium, and titanium, to achieve special desirable properties.

Nickel-iron alloys containing up to about 25 percent nickel are noted for their nonmagnetic properties, and are used for transformer, motor, and generator parts. On the other hand, nickel-iron alloys containing 45 to 80 percent nickel are highly magnetic and are of considerable value in the manufacture of radio and telephone equipment. A nickel-iron alloy that contains about 36 percent nickel has a very low coefficient of thermal expansion, and is widely used in the manufacture of such items as measuring tapes, precision instruments, and watches.

Another group of alloys, the so-called nonferrous alloys in which iron is not used or is present only in small quantities, accounts for 25 to 30 percent of nickel consumed. Included among these are Monel metal, the cupro-nickel alloys, nickel silver, and Inconel. Monel metal, the most important of these commercially, is composed of approximately 67 percent nickel, 30 percent copper, and minor amounts of iron and manganese. It is a strong, silvery white metal which is of special value because of its resistance to corrosion by many acids, atmospheric influences, industrial corrosives, and sea water. Thus it is widely used in the manufacture of equipment in the food, chemical, petroleum, and pharmaceutical industries, and in marine service.

The cupro-nickel alloys contain copper alloyed with less than 50 percent of nickel. These alloys are used especially for condenser tubes and steam turbine blades in marine service, and in petroleum refineries for heat exchanger tubes. The 75 percent copper-25 percent nickel alloy is used in United States 5-cent coins.

Nickel silver is an alloy of copper, nickel, and zinc that closely resembles silver. It has good resistance to corrosion, and is largely used for food equipment, marine fittings, musical and dental instruments, and slide fasteners.

Inconel is a nickel-chromium-iron alloy that combines all of the good qualities of nickel with the oxidation resistance of chromium. A typical formula is 80 percent nickel, 13 percent chromium, and 7 percent iron, although these proportions are varied for special metallurgical needs and small amounts of columbium and titanium are substituted in part for nickel for better high temperature service. Inconel is widely used in equipment for manufacture of dairy products, wines, fruit juices, caustic alkalies, fatty acids, dyestuffs, and edible oils.

Numerous heat- and corrosion-resistant nonferrous alloys contain nickel alloyed with one or more of the following metals: chromium, cobalt, molybdenum, iron, tungsten, columbium, titanium, and aluminum. The

maximum temperatures at which these alloys can be used range up to about 2,100° F.; thus they have a wide variety of uses, such as in furnace construction, high-speed tools, and gas turbine and jet engines.

The iron-aluminum-nickel-cobalt permanent magnet alloys commonly contain 15 to 30 percent nickel. They have wide use in the vital parts of motors, generators, radio speakers, telephone receivers, microphones, magnetos, and galvanometers. The most important electrical-resistance alloy contains 80 percent nickel and 20 percent chromium, and is used largely as the heating elements of numerous household and industrial appliances.

Pure nickel metal finds applications in food processing equipment, chemical apparatus, cyanide fusion pots, television and radio equipment, variable time-fuse tube electrodes, and many other items. It is used for electroplating other metals to produce thin nickel coatings for decorative and protective purposes, and as undercoatings for chromium plating.

Finely divided nickel metal and nickel salts are used as catalysts in the hydrogenation of vegetable oils to produce oleomargarine, in purifying gas, and in producing high-octane motor fuels.

The estimated total nickel consumption in the United States during 1956 was 126,000 short tons.

#### Marketing Problems and Prices

There are no markets for nickel ores or concentrates in California, and the only nickel processing plant in the western United States is that of the Hanna Nickel Smelting Company at Riddle, Oregon, which is especially designed to handle the silicate ores from adjacent Nickel Mountain. Thus it is to be expected that any nickel mining operation developed in the state will require construction of processing facilities.

Prices quoted by International Nickel Co., Inc., the largest producer, for electrolytic nickel, f.o.b. Port Colborne, Ontario, have gradually increased from 35 cents per pound in 1947 to 74 cents per pound in January, 1957. However, during the past few years, particularly 1955-56, increasing nickel consumption for defense purposes has led to severe shortages for civilian production. As a result, the metal has been purchased by fabricators within the United States for prices as high as \$3.50 per pound. On September 14, 1956, American Metal Market reported that steel mills were offering \$1.75 to \$2.75 per pound for scrap and secondary nickel. In fact, 18-8 stainless steel scrap, containing only 8 percent Ni, was being sought at \$1.75 per pound of contained nickel. Nickel platers were reported paying \$3.00 to \$3.50 per pound for nickel anodes. These prices contrasted with the virgin nickel price of 64½ cents per pound published by one company and \$1.25 per pound published by another.

#### Mining Methods and Treatment

Virtually all of the known mining methods have been used in the mining of nickel. The large sulfide deposits at Sudbury are most commonly mined by open-pit or glory-hole methods in the initial stages. When underground work becomes necessary, such methods as shrinkage stoping, cut and fill, square set, and blast-hole methods are used to suit local conditions. However, where practicable, large-scale caving methods have been



found to be the most economical types for underground mining and are widely used.

Lateritic ores, which occur as blanket deposits with little overburden, are mined only by open-cut methods.

Many methods are also used to recover nickel from ores. The sulfide ores mined by International Nickel Co. at Sudbury are first crushed and ground to about 65 mesh, then concentrated by flotation. Two kinds of concentrates are produced: a copper concentrate, high in copper and low in nickel, and a nickel concentrate that is low in copper. The nickel concentrates are roasted to remove part of the sulfur. The sulfide matte made from this calcine is put through a bessemerizing operation, in which it is blown to a point where about 15 percent of the mass is a copper-nickel alloy, the remaining 85 percent being combined nickel and copper sulfides. Following the blowing operation, this matte is allowed to cool slowly under carefully controlled conditions. While cooling, the molten mass crystallizes out into three separate phases: (1) a copper-nickel alloy containing approximately 95 percent of the precious metals, such as gold and platinum, present in the matte; (2) a copper sulfide containing about 1 percent nickel; and (3) a nickel sulfide containing about 1 percent copper. This mass is crushed to minus 325-mesh and passed through a magnetic separator to extract the magnetic nickel-copper alloy containing the precious metals. The sulfide fraction is treated by flotation to separate nickel sulfide from copper sulfide. The magnetic alloy is dissolved and its nickel, copper, and precious metals content recovered by electrodeposition. The copper sulfide goes to a copper smelter, and the nickel sulfide is roasted and sintered to produce nickel oxide. The nickel oxide is marketable for steel-making, or it can be sent to a refinery for electrolytic or Mond process reduction to pure nickel (Materials Survey—Nickel, 1952, p. VII 22).

Lateritic nickel ores cannot be concentrated by milling, so the entire ore as mined must be put through a smelting or wet recovery process in order to recover the nickel. Several processes have been used in treatment of these ores, but extensive research in recent years has developed new processes as well as refinements for those already in use. Many of these efforts have been directed toward finding economic methods of recovering the cobalt, chromium, and iron in addition to the nickel present in lateritic ores. Unfortunately, details of most of the recent developments have not yet been made available through publication.

The garnierite-rich lateritic ores have usually been processed by smelting techniques. In New Caledonia, selectively mined high-grade ores, containing 3 percent to 5½ percent nickel, are ground and mixed with gypsum, then briquetted. The briquettes are smelted in a blast furnace with flux and coke. Decomposition of the gypsum results in a fusible nickel sulfide matte containing about 45 percent nickel, 40 percent iron, and 15 percent sulfur. This matte is bessemerized to produce a matte containing about 76 percent nickel and 23 percent sulfur. The final high-grade matte is shipped to France for reduction to the metal (Dennis, 1954, p. 353).

At Riddle, Oregon, the garnierite-rich ore is reduced to ferronickel by a recently developed electric smelting method known as the d'Uguine process (British Patent

713,713, Aug. 18, 1954). According to Chemical Abstracts: \*

"Nickel is extracted from low-grade ores, as an Fe-Ni alloy, by mixing successive charges of molten ore with molten Fe and periodically withdrawing a part of the metal. Exothermic heat from oxidation of added Si or Al compensates for heat losses. Formation of CO from C addition causes bubbling. Treatment of ore containing NiO 1.5, FeO 35, and SiO<sub>2</sub> 35 percent with Fe and Fe-Si in a converter reduces the ore to 0.20 percent Ni and after processing gives a 30 percent Ni alloy."

The iron-rich nickeliferous laterite at Nicaro, Cuba, is treated by ammonia leaching methods for recovery of the nickel (Lutjen, 1954). The ore, containing about 1.4 percent nickel, is finely ground in ball mills, then calcined in reduction furnaces to reduce the nickel to metal. This calcine is leached in an 11 percent ammonia-ammonium carbonate solution, which dissolves the nickel and oxidizes the iron to a gelatinous ferric hydroxide precipitate. After filtering, basic nickel carbonate is precipitated by blowing steam through the solution. The nickel carbonate is filtered off and calcined in a rotary kiln to produce nickel oxide, the final product.

Ammonia leaching methods are also used for recovery of nickel, copper, and cobalt from sulfide concentrates at some of the Canadian mines. Forward (1953) has described a recently developed pressure leaching system used for processing sulfide concentrates from the Sherritt Gordon mine at Lynn Lake, Manitoba.

The U. S. Bureau of Mines has recently carried on considerable research directed toward the recovery of nickel from low grade ores by smelting techniques, and has published preliminary reports on some of the results (Hundhausen, et al., 1954, pp. 9-15; Cremer, 1954; Banning and Arable, 1955; Shelton, 1956).

Pure nickel metal is recovered from the oxide by two methods, the Mond process, and electrolytic refining (Dennis, 1954, chap. 7; Materials Survey—Nickel, 1952, chap. 7). The Mond process is based on the property of nickel to combine with carbon monoxide to form nickel carbonyl (Ni(CO)<sub>4</sub>), a volatile compound that is stable below 60° C. but breaks down to the original reactants on heating to 180° C. The impure nickel oxide is reduced in special vertical gas-tight towers to yield metallic nickel powder, which is passed to volatilizing towers. Here the nickel powder passes downward through a stream of rising carbon monoxide, the temperature being maintained at 50° C. The volatile nickel carbonyl formed is passed through a continuously circulating mass of nickel shot maintained at 180° C. At this temperature nickel carbonyl is decomposed, the nickel being deposited on the shot.

Electrolytic refining is accomplished by using an electrolyte composed of a solution of nickel sulfate and chloride containing about 40 grams of nickel per liter (Dennis, 1954, p. 352).

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## NITROGEN COMPOUNDS

BY WILLIAM E. VER PLANCK

Although nitrogen is a comparatively abundant element, much of it exists in the atmosphere as a nearly inert gas that can be combined with other elements only with difficulty. Nitrogen comprises 78 percent of the atmosphere by volume. All animal and vegetable matter contains nitrogen compounds, and nitrogen compounds are concentrated in coal. Economic deposits of nitrogen minerals are known only in Chile.

The consumption of nitrogen compounds in the United States is the equivalent of roughly  $3\frac{1}{2}$  million tons of ammonia ( $\text{NH}_3$ ) a year, nearly 85 percent of which was manufactured by domestic plants in 1953. The principal supply was synthetic ammonia manufactured from hydrogen and nitrogen gas, and most of the remainder was ammonia compounds obtained as by-products in the manufacture of coke from coal. The remainder of the United States supply, which is imported, includes ammonium sulfate, ammonium nitrate, ammonium phosphate, and calcium cyanamide manufactured in Canada, calcium nitrate manufactured in Norway, and natural nitrates from Chile. Imports from Chile amounted to less than 4 percent of the supply.

**Deposits of Nitrate Minerals.** Sodium nitrate ( $\text{NaNO}_3$ ) is produced on a large scale from natural nitrate deposits in Chile. The deposits occur in a belt a few miles wide and over 400 miles long that lies between the coast range and the Andes. The area between the two mountain ranges is one of the most arid in the world. The nitrates are found in gently dipping deposits of gravel or sand cemented by soluble salts. Caliche is the local term used for material containing recoverable amounts of nitrate. The caliche rarely crops out. Typically it is overlain by gravel or sand rich in chlorides and sulfates, and it lies on gravel or fractured rock that does not contain soluble salts. The deposits of caliche are very irregular. They range in thickness from 6 inches to 25 feet and are covered by 2 to 3 feet of overburden. Physically, the caliche is hard and compact. A typical analysis follows (Rogers, A. H., and Van Wagenen, E. M., 1918, p. 11):

	Percents
$\text{NaNO}_3$ .....	14-25 (sometimes up to 40)
$\text{KNO}_3$ .....	2-3
$\text{NaCl}$ .....	8-25 (sometimes 50-60)
$\text{Na}_2\text{SO}_4$ .....	2-12
$\text{CaSO}_4$ .....	2-6
$\text{MgSO}_4$ .....	0-3
$\text{Na}_2\text{B}_4\text{O}_7$ .....	1-3
$\text{NaIO}_3$ .....	0.05-1.0
$\text{NaClO}_4$ .....	0.1-0.5
Insoluble .....	to make 100

In the recovery of nitrates, the caliche is first drilled, blasted, and excavated, generally by open cut methods. The caliche is then crushed to a fairly coarse size, 1 inch to  $\frac{1}{2}$  inch, and leached with hot mother liquor returned from a later step in the process. The nitrate-rich liquor from the leaching tanks is cooled, and sodium nitrate crystals precipitate. Chilean nitrate is guaranteed to contain 95.5 percent sodium nitrate and a maximum of 2 percent moisture, 1.5 percent sodium chloride, 0.75 percent potassium chloride, and 0.5 percent borax.

Two processes are used to produce the sodium nitrate, the Shanks process and the Guggenheim process. Shanks process plants have capacities of 10,000 to 110,000 tons of sodium nitrate a year. The minimum grade of ore that can be used is 12 to 13 percent  $\text{NaNO}_3$ . Much hand labor is required, the consumption of fuel is high, and losses in all steps from mining through refining sometimes total as much as 50 percent. Guggenheim process plants are highly mechanized and have capacities of more than 500,000 tons of sodium nitrate a year. Ammonia refrigeration is used for cooling the nitrate-rich solution, and the maximum use is made of waste heat recovered. Losses of nitrate in the process are low. The minimum grade of ore that can be used is 8 percent  $\text{NaNO}_3$ . In recent years the production of nitrates in Chile has been in order of one to 2 million tons per year, a little less than half of which is shipped to the United States. Reserves are not generally known but are believed to be adequate for many years.

**Sources in California.** No commercial deposits of natural nitrogen compounds have been found in California, although traces of sodium nitrate have been found in certain playas and in efflorescent deposits throughout the southeastern desert. An exhaustive search of these occurrences was undertaken by the United States Geological Survey during and following World War I. The most promising deposits were in the southern part of the Amargosa Valley, Inyo and San Bernardino Counties, where two areas totaling 168 acres were estimated to contain 1,980 tons of sodium nitrate. The nitrate occurs with sodium chloride and other salts in a layer of caliche about 5 inches thick that rests on folded Tertiary lake beds. The caliche is unevenly distributed and averages less than 2.5 percent sodium nitrate (Noble, 1922, p. 91).

The present most important nitrogen compound in California is synthetic ammonia produced at three plants in the San Francisco Bay area and two in the Los Angeles area. Ammonia is synthesized from hydrogen and atmospheric nitrogen at high temperature and pressure in the presence of a suitable catalyst. Four of the plants obtain hydrogen from natural gas, and the fifth uses hydrogen obtained as a by-product in the electrolysis of sodium chloride brine. Ammonium salts and nitric acid are produced from ammonia at these and other plants in the state. Ammonium sulfate is produced as a by-product of coke manufacture at the Fontana plant of the Kaiser Steel Company, and a petroleum refinery in the Los Angeles area recovers an additional amount from waste products.

**Uses.** Nitrogen compounds are of economic value because nitrogen is a plant food that is essential for the healthy growth of plants, and because nitric acid is an important chemical raw material used in the manufacture of explosives and by other chemical industries. The most important use of nitrogen compounds is for fertilizer. In 1954, the fertilizer used on California farms contained 162,060 tons of nitrogen. Explosives require additional quantities and during times of war the de-



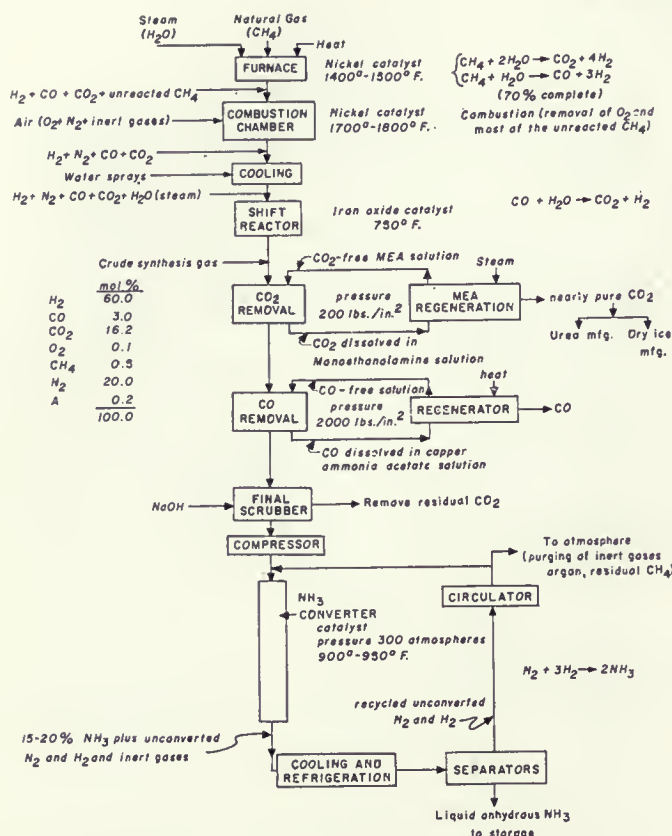


FIGURE 1. Flow chart showing the production of synthetic ammonia from synthesis gas produced by the steam-methane process.

mand for nitrogen compounds to be used for explosives may exceed the demand for fertilizers. Smaller quantities are consumed in the manufacture of plastics and synthetic fibers, and in pulp processing.

California soils are in general more deficient in nitrogen than in other plant foods. In addition to the nitrogen removed by crops, nitrates are leached from soils, and gaseous nitrogen released by bacterial action also is lost. It is thought that nitrogen must be in the form of nitrate to be available to plants. The nitrogen content of manure and other organic compounds as well as that of

ammonium salts and calcium cyanamide is, however, readily converted to the nitrate form in the soil by bacterial action. In California most of the nitrogen added to soils is in mixed fertilizers, but large tonnages of ammonia, ammonium sulfate, ammonium nitrate, ammonium phosphate, sodium nitrate, calcium nitrate, and calcium cyanamide also are used.

**Prices.** In 1955 the price of Chilean sodium nitrate was \$47.75 per ton in bulk at Pacific Coast ports. The price of anhydrous ammonia was \$85-\$88 per ton, and the price of synthetic ammonium sulfate in bulk was \$42-\$46 per ton.

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## PEAT \*

By CHARLES W. JENNINGS

Peat deposits are widespread in California, but only in four areas are the deposits known to be of suitable quality, large enough, and so located to be of present commercial value. These areas, from which substantial amounts of peat have been mined and then processed, are the Sacramento-San Joaquin Delta area, Orange County, Modoc County, and Santa Cruz County.

In the United States peat is used mostly as a soil conditioner and in mixed fertilizers. Very small amounts are used as mull or litter material for domestic animals, as packing material, and in chemical applications such as filtering and tanning. Although peat has been used as a fuel in other countries, the abundance of higher rank fuels in the United States has kept peat out of the domestic fuel industry.

During 1953, 9,196 tons of peat valued at \$73,897 were produced in California. To help meet the increasing demand for agricultural peat, large quantities of peat moss were shipped into California primarily from Canada with occasional shipments from eastern states. The major peat producers in California are initiating expansion programs to meet this demand.

**Geologic Occurrence.** Peat is an accumulation of partly decomposed and disintegrated vegetal matter representing the first stage in the metamorphism of plants to coal. It forms in undrained depressions, plains, or river deltas that contain environments favorable to luxuriant growth of peat-forming plants. The plants range from woody shrubs and trees of swamps, to mosses, sedges, reeds and grasses of marshes. Poor drainage is essential in the formation of peat, because standing water largely excludes oxygen and prevents complete decay, thus enabling the carbonaceous matter to be preserved.

The type of vegetation that accumulates determines the type of peat that is formed. The most valuable and sought-after commercial peat is formed from aquatic mosses. Most of this material is either a sphagnum or hypnum moss, and is known in the industry as peat moss. Other commercial grades of peat include reed or sedge peat, and peat humus which is a soil high in organic matter. Most of the peat produced in California is classified as peat humus and reed or sedge peat. A high-grade peat moss, however, is recovered from a single bog in Modoc County in northern California.

The principal nations that contain most of the world's peat and the extent of their peat-bearing areas are as follows:

U. S. S. R.	65,000 square miles
Canada	37,000 square miles
Finland	30,000 square miles
Sweden	19,000 square miles
United States	11,200 square miles

Other countries having smaller peat reserves but which produce substantial amounts of peat include: Ireland, Netherlands, Denmark, Germany, and Norway. The estimated world production of peat in 1953 was 53 million metric tons. Approximately 85 percent of this amount

was produced in the U. S. S. R. where large quantities are used in electric power generation.

The United States contains extensive reserves of peat in at least 26 states. The northern region embracing Iowa, New England, and those states bordering on the Great Lakes contains 80 percent of the total deposits of the country. Although the Pacific Coast States have less than 1 percent of the nation's total, Washington led all states in peat production and in the number of active operations in 1953.

In Minnesota and Wisconsin, peat has been derived from mosses, grasses, sedges, shrubs, and trees, and the deposits vary in texture from fibrous in the top layer to plastic at the bottom. The peat deposits of Iowa, Illinois, Indiana, Ohio, Pennsylvania, and New Jersey are of similar texture, although generally more fibrous. Sphagnum peat abounds in the deposits of northern Minnesota, Wisconsin, and Maine, and also is found in other New England States. In the salt marshes of the New England coast, sedges are dominant. Both coniferous and deciduous trees contributed a large portion to the vegetable matter of the peat along the Atlantic coast south of New Jersey, and these deposits contain little sphagnum. Florida Everglades peat was formed largely from saw grass and sedge.

**Localities in California.** The largest peat deposits in California are found in the Sacramento-San Joaquin Delta area. Here peat and peaty muck deposits cover an estimated 400 square miles most of which are under cultivation. Peat humus deposits in the Huntington Beach area in Orange County are small compared to the Delta area, but production is comparatively high. A peat bog in Modoc County supplies peat moss. Peat has been mined in the past from San Diego, Santa Cruz, and San Bernardino Counties, and U. S. Soil Survey maps show peat and peaty muck occurring in Round Valley, Inyo County; near the mouth of Salinas River, Monterey County; along San Antonio River and south of the mouth of Santa Maria River, Santa Barbara County; and in various sites in Siskiyou and Humboldt Counties (U. S. Department of Agriculture, 1919-44).

In the Sacramento-San Joaquin Delta area in central California, peat is exposed over an area of about 250,000 acres (Weir, 1950). These highly organic soils are said to comprise the second largest continuous body of peat land in the United States, exceeded only by the Everglades in Florida. With the exception of a few small areas, the entire Delta has been reclaimed from tule swamp and is under cultivation. The center of the Delta is composed of islands which are surrounded by interlacing channels of the two major rivers. In portions of this area the peat is 40 feet or more in depth (Water Project Authority, 1956). All of the channels surrounding the islands are navigable to barges and other freight-carrying craft.

Cosby (1941) mapped the organic soils of this region and divided them into five series. Of these Correra peat represents the extreme in raw, unaltered, parent organic material. Correra peat, which occurs mainly on marsh

\* Extracted in part from *Peat*, by Lewis T. Braun, in California Div. Mines Bull. 156, 1950.



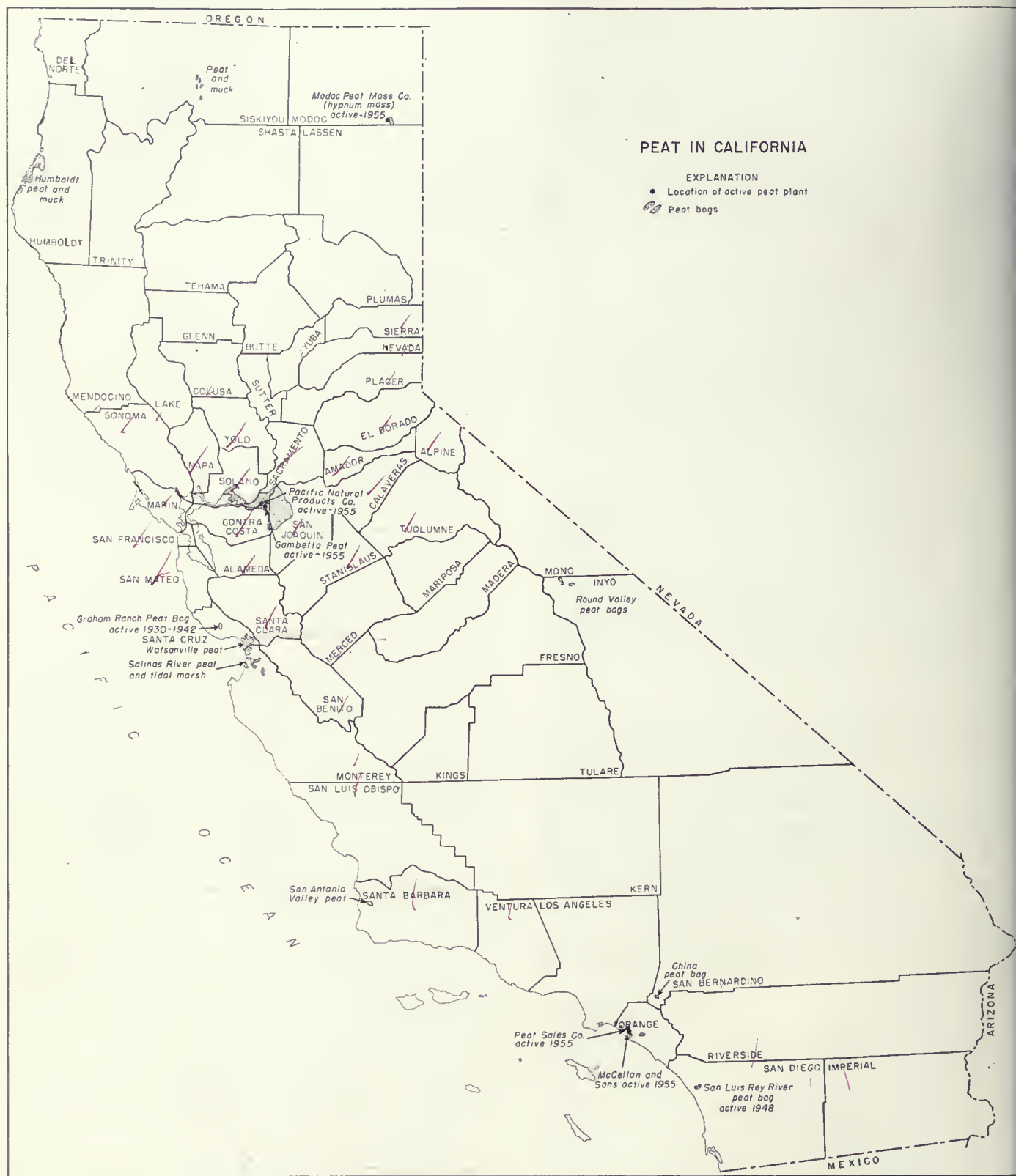


FIGURE 1. Index map of California showing distribution of peat. (Ed. note: In 1955 the name Pacific Natural Products Company was changed to Vita-Peat Corporation.)





FIGURE 2. Grinding and stockpiling peat at the Vita-Peat Corporation's plant on Bethel Island in the Sacramento-San Joaquin Delta area.

and, is estimated to underlie 5,312 acres in the Sacramento-San Joaquin Delta area. Cosby describes this peat as follows:

Correra peat consists of practically unaltered virgin deposits of peat characteristically having two layers—a comparatively thin layer of material derived from tule, or bulrush, overlying a deeper accumulation of fibrous remains of reed. . . .

By far the larger part of Correra peat remains unreclaimed and continues to support a cover of native plants. In some localities a dense and almost pure stand of tules occurs, although in general, some reeds, willows, and herbaceous plants are also included. . . .

In general, the two layers of Correra peat have the following profile characteristics:

Top layer (10' to 20' thick)	Brown fibrous-matted tule peat, abundant light-brown small fibrous roots and dark-brown or almost black shiny tule rhizomes. Small quantities of dark brownish-gray finely divided altered plant material. Has pH of about 5.0 and is about 80% organic.
Bottom layer (30' to 40' thick)	Brown or light-brown raw fibrous-matted tule-reed peat similar to above peat but containing many identifiable stems and roots of reeds, which become even more numerous in the lower part. Grades into underlying brown, softer and more altered reed peat.

In 1955 Correra peat was being dredged from Frank's Tract in the San Joaquin Delta area by the Vita-Peat Corporation (formerly Pacific Products Company). Bethel Island, California. Frank's Tract, lying under 6 to 8 feet of fresh water, was farm land protected by levees prior to 1937 when the area was flooded by levee breaks. The submerged peat is preferred by the operators because it is believed to be seed free; however, adequate testing of the marsh peat in this respect has not been attempted. The peat, classified by the U. S. Bureau of Mines as a reed or sedge peat, is mined by means of a floating clamshell dredge and is transported by barge to a stockpile on neighboring Bethel Island. After a period of one to two months, the large fibrous lumps are spread to dry in the sun, then ground to various grades for horticultural and other purposes. The finished product is sold through exclusive distributorships in either bulk truckloads, or in one-, two-, or five-cubic-foot poly-

ethylene-treated bags for the retail trade in California, Nevada, Arizona, Utah, Oregon, and Idaho. In 1954 the company dredged more than 25,000 cubic yards.

In the fall of 1955, a new peat operator, Mr. P. J. Gambetta, was starting a peat operation from another part of Frank's Tract. A large barge of 500 cubic yard capacity was being used to transport the peat to a drying yard at Indian Slough. Approximately 1,700 cubic yards had been stockpiled.

A peat bog north of *Huntington Beach, Orange County*, has been the source of peat for the past 30 years. The bog, which is a naturally filled-in lake, is estimated by the operators to average about 15 feet thick and covers about 35 acres of dry land. The material is classified as peat humus and is sold for use as a soil conditioner. Two operators are currently mining peat at this locality: the Peat Sales Company, D. M. Callis, Jr., 17581 Gothard Road, Huntington Beach; and R. W. McClellan and Sons, 151 Commercial Way, Costa Mesa. The peat is mined by dragline and scrapers, and a mill on the site crushes the peat and screens out reeds and rocks. The



FIGURE 3. Unloading peat from barge at Frank's Tract in Sacramento-San Joaquin Delta area.



Table 1. Specifications for peat purchased by the federal government (from Federal Stock Catalog Q-P-166)

	Composition	Texture	Deleterious substances	Acidity (pH)	Moisture content (by weight)	Water holding capacity (by weight)	Color	Ash content
PEAT MOSS-----	Poorly decomposed stems and leaves of Sphagnum moss	Porous fibrous to spongy fibrous. Crumbly or compact, homogeneous.	Decomposed colloidal residue, wood, sulfur, iron.	Not less than 3.5. Not more than 5.5	Air dry. Not more than 35%	Oven dry basis. Not less than 1,100%	Brown Gray Yellow Red	
Horticultural grade		Finely shredded dust size to wheat bran size.						
Poultry litter		Mediumshredded lumpy; as large as walnuts.						
Stable bedding		Coarsely shredded. May contain larger lumps.						
PEAT HUMUS (Reed muck or sedge muck)	Finely divided plant debris in fairly advanced state of decomposition.	Granular, uniform size, free from hard lumps.	Wood, sulfur iron.	Not less than 5.0. Not more than 7.5.	Not more than 55%	Oven dry basis. Not less than 100%	Dark brown to black	Not more than 15%
REED PEAT OR SEDGE PEAT	Moderately decomposed stems and roots of rushes, coarse grasses, sedges, reeds, canes, etc.	Coarse or finely fibrous.	Wood, decomposed colloidal residue, sulfur, iron.		Not more than 50%	Oven dry basis. Not less than 350%	Brown	Not more than 10%
Acid grade				Not less than 4.5. Not more than 5.5				
Nearly neutral grade				Not less than 5.5. Not more than 7.5				

finished product is loaded into dump trucks, delivered in bulk loads, and marketed from the Mexican border to Ventura County.

The Modoc Peat Moss Company recovers hypnum peat moss from a bog in *Jess Valley, Modoc County*, near Likely, and is the only commercial peat moss mining operation in California. The bog is free of tree and shrub growth and contains no alluvial deposits. The marketable moss extends from the surface down to two or four feet, and is underlain by a highly organic substratum. The Soil Survey map (U. S. Department of Agriculture, 1931) shows approximately 1,280 acres (two sections) underlain by peat and peaty muck. Because of the high elevation (6,000 feet) and the rigorous winters, the bog is worked only from July through November.

The peat moss is scraped from the bog onto levees where it is air dried for about four weeks, and the dried material is then collected and trucked to Likely for bulk rail shipment. The 1955 production is estimated to have been about 10,000 cubic yards. The Modoc Peat Moss Company maintains an office at 604 Mission Street, San Francisco.

In *Scott Valley, Santa Cruz County*, 5 miles north of the city of Santa Cruz, a peat deposit was worked for about 12 years starting in 1930 (Hubbard, 1943). About 1,000 tons of peat were produced annually, and the peat was loaded by hand shovel. The dried peat was pulverized in a hammer mill and stored in a large barn to meet orders for delivery by dump truck. The peat was classified as a sedge peat and ranged in depth from 2½

to 9 feet. The bog covered about 15 acres of the Graham Ranch.

In 1948 a small amount of peat was mined in *San Diego County* from a bog near the Camp Pendleton Naval Reservation (Roy Kepner, 1956, San Diego County Department of Agriculture, Division of Natural Resources, personal communication). The bog was adjacent to the San Luis Rey River, and lay largely beneath a pond which had been drained. A forty-foot test pit indicated peat the entire depth. The mined material contained approximately 85 percent water and was composed largely of decomposed tules and other aquatic vegetation. Leasing problems and mining difficulties caused the project to be abandoned.

A small amount of peat was mined during the early 1920's near Chino, San Bernardino County, and its occurrence is mentioned in the U. S. Geological Survey Bulletin 728 (Soper, 1922).

*Utilization.* The principal use of peat is as a soil conditioner. Peat contains a large percentage of fibrous and porous organic matter (humus) which improves the physical structure of the soil and promotes plant development when used in large enough quantities. Peat mixed with heavy clay soils makes them more granular, less plastic, and consequently more permeable to water, air, roots and microorganisms. In sandy soils peat helps bind the soil particles, retards excessive percolation, and makes the soils more retentive of moisture and nutrients. Contrary to popular belief, peat is not a fertilizer, and the nitrogen that it contains (3 percent or more in some





FIGURE 4. Scraping peat from bog at Huntington Beach area, Orange County.

peat) is not readily given up as a plant food like the "soluble nitrogen" of artificial fertilizer. Peat is suitable for preparing soil for plants that prefer an acid condition, such as rhododendrons, azaleas, camellias and gardenias. Peat is commonly mixed with sand and loam soil in the preparation of potting mixtures or in the germination of seeds.

The second largest market of peat is as an ingredient or filler in mixed fertilizers in which it acts as a carrier for the primary nutrients—nitrogen, phosphoric oxide, and potash—not as an agent for supplying plant food. Well-decomposed peat dried and ground is ordinarily used for this purpose. Because of its moisture-absorbing qualities, fibrous peat is used as a litter material for bedding livestock, and its deodorizing capacity makes it useful in stable and poultry yards. Nurserymen, gardeners, and others use peat as a packing material for plants, fruit, vegetables, eggs, fish bait, and fragile materials. Other uses of peat include filtering agents, dye stuffs, tanning substances, and as absorbent in surgical dressings, but the quantities so used are small.

In several European countries, peat is used as a fuel, but it is not so used in the United States because of ample supplies of superior fuels with much higher calorific values. Other products derived from peat in certain European countries, but not produced on a large scale, include montan wax, peat coke or char, gas, and tar products.

**Markets.** The demand for peat in California has risen sharply in the past 5 years. The value of the peat produced in 1953 was \$73,900—more than twice the value produced in 1949 which was reported as \$35,200 (U. S. Bureau Mines, 1949, 1953). California ranked seventh in production among the 18 states producing peat in 1953. Although the United States contains ample reserves of peat, large quantities of peat moss are imported annually, principally from Canada, Germany, and Netherlands. The low cost of labor in foreign countries and the low cost for transporting the peat (used as ballast in ships) enable the imported peat to compete with domestic sources. Imports of peat moss, the only type imported, are subject to a 25-cent duty per ton.

The wholesale price (f. o. b.) of peat in California ranges from about \$3.00 to \$4.00 per cubic yard depending on the type of peat, and whether it is ground and screened or unprocessed.

The federal government purchases a certain amount of peat primarily for horticultural purposes provided the peat meets their specifications. These specifications are outlined in table 1. Methods of sampling and tests are explained in the Federal Stock Catalog Q-P-166 which may be obtained from General Services Administration, Business Service Center, Region 3, Seventh and D Streets, S. W., Washington 25, D. C. Opinions differ as to the relative value of certain kinds of peat, and nurserymen and growers have their own preferences. Except for the peat sold to the federal government and some state agencies, the peat industry does not have standard specifications or standard tests for grading peat.

Recent improvements in bagging materials, including polyethylene products and other paper or textile bags treated with resins, make packaging more feasible, permit shipment over long distances, and allow storage for lengthy periods without deterioration of the bags or the product.

Peat producers face a continuing problem of quality control. For ordinary greenhouse use and for home garden purposes, peat should be free from hard lumps and from excessive salt or alkali. Peat with brittle stems and strawlike texture soon breaks down to form a dust and is considered inferior. Peat materials that are even in texture, fibrous, and free from dirt and alkali salts should prove satisfactory. Actual growing tests will help demonstrate the value of the different kinds and grades of peat.

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# PETROLEUM

By CHARLES W. JENNINGS

California's crude oil production reached an all-time high in 1953, when it exceeded one million barrels per day or a total of 367,292,000 barrels for the entire year. After a temporary decrease in 1954 and part of 1955, production began to increase in late 1955 and attained 981,000 barrels per day at the close of the year. California stands second only to Texas in crude oil productive capacity and provides about 15 percent of the nation's oil. During 1954, more exploratory wells were drilled in California than in any previous year and, in late 1955, exploratory drilling was active in every major sedimentary basin in the state and in the offshore waters along the coast. California's offshore oil deposits have an estimated potential production of more than 4 billion barrels. In 1955, the State legislature passed a tidelands oil bill which has stimulated offshore oil exploration primarily by no longer restricting offshore drilling to only those fields threatened by drainage from onshore wells. Deep drilling in onshore fields has become more common and in recent years has led to most of the new discoveries and most of the additions to reserves.

## GEOLOGIC OCCURRENCE

The important discoveries of petroleum in California have been restricted to certain areas in the San Joaquin Valley, the southern Coast Ranges, the Transverse Ranges and the Los Angeles basin. This is not accidental, but is attributable to the fact that commercial accumulations of petroleum form only in special geologic environments. Such environments pertain in a relatively small part of the area of California.

*Origin of Oil.* An estimated 99 percent or more of all the known oil in the world occurs within or in close proximity to sedimentary rocks which either contain abundant organic remains or were deposited under conditions that supported abundant plant and animal life

(Hoots, 1941). Although small quantities of oil have been attributed to inorganic origins, the weight of chemical and geological evidence has led to a general acceptance of the concept that all commercial deposits of petroleum and gas originated in organic matter buried in sediments during past geologic ages. The processes by which such organic matter is transformed into petroleum are not completely understood, but such factors as bacterial action, depth of burial, temperature, pressure, catalysts, and perhaps radioactivity, are contributing causes.

*Reservoir Rocks.* After formation, petroleum must migrate to and be trapped in a permeable and porous reservoir rock before a potential oil pool can exist. When the source muds are buried beneath other sediments, the accumulating weight is believed to gradually compact the lower beds, and the petroleum and other enclosed liquids are squeezed into more permeable rock such as sandstone. Then the oil and gas migrates under the action of capillarity, gas pressure, and hydraulic pressure through the reservoir rock. Where suitable traps exist, the oil is concentrated. In general, an oil reservoir rock must have sufficient pore space to contain large quantities of fluids and the fluids must be able to flow through it; that is, a reservoir rock must have high porosity and permeability in order to yield petroleum. An estimated 98 percent of the oil produced in California is obtained from fields with sandstone reservoir rocks. A few fields in the Los Angeles basin yield part of their oil from Miocene conglomerates composed of schist fragments or from reservoir rocks composed of fractured schist of Jurassic (?) age. Fractured schist also forms the reservoir rock in one pool in the Edison field in the San Joaquin basin. Fractured chert or shale of Miocene age yields all or part of the oil in the Santa Maria basin fields and comprises one of the reservoir rocks in at least 3 fields in the San Joaquin basin.

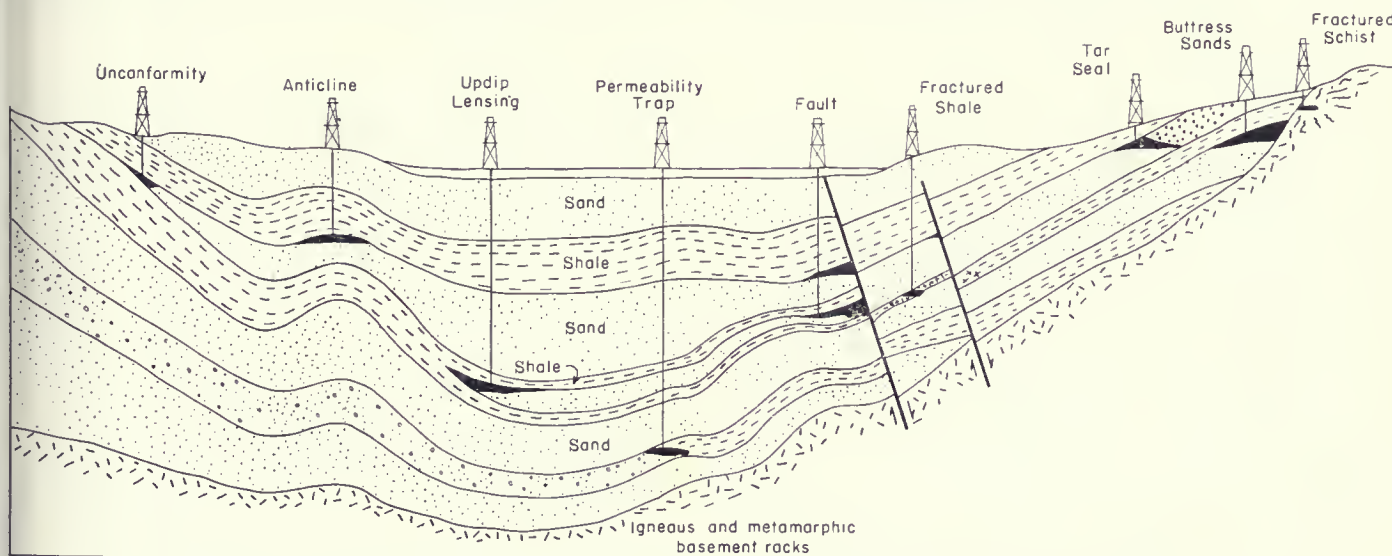


FIGURE 1. Generalized cross-section showing representative types of oil traps found in California.



Table 1. Production of crude oil in California by geologic ages.\*

Geologic age	No. of pools	Cumulative production on 1/1/55 (thousand bbls.)	Production 1954 (thousand bbls.)	No. of producing wells 12/31/54
Pleistocene	7	345,394	3,833	2,470
Pliocene	149	4,845,813	118,945	13,852
Miocene	405	4,400,188	195,773	14,890
Oligocene	37	135,440	13,332	923
Eocene	39	326,198	21,610	523
Cretaceous	3	2,520	14	2
Basement	3	25,053	2,155	126
Unclassified	7	3,832	203	78
California total	650	10,084,438	355,865	32,864

\* From Conservation Committee of California Oil Producers, 1955.

An outstanding feature of the reservoir rocks of many California oil fields is their enormous thickness or vertical extent. The aggregate thickness of the oil producing zones in a single field commonly is measured in thousands of feet, and, in effect, is equivalent to several normal fields of other regions piled one upon another (Carter, 1954). This results in some astonishing per acre recoveries. Long Beach oil field, for example, has produced more than 600,000 barrels per acre and is one of the largest producing oil fields in the state.

Oil in California is withdrawn from reservoir rocks that range in age from Pleistocene to pre-Cretaceous. Table 1 shows the number of pools and their production arranged by geologic ages. Most of this production is now obtained from formations of Miocene age although most of the cumulative production to date has been from rocks of Pliocene age.

**Oil Traps.** A trap is any combination of geologic features that will stop the upward and lateral migration of petroleum and allow it to collect in a limited area. A trap may be the result of structural deformation, stratigraphic conditions, or a combination of the two. In order to be effective, the trap must lie under an essentially impervious caprock or other seal. The known oil traps in California fields may be classified as follows:

- I. Structural traps (tectonic causes)
  1. Anticlinal
  2. Fault
  3. Fracturing
  4. Combination of above
- II. Stratigraphic traps (caused by irregularities in rocks when deposited)
  1. Depositional (lensing, buttressing)
  2. Erosional (truncation—unconformities)
  3. Cementation (tar seal, porosity-permeability factors)
  4. Combination of above
- III. Combination structural—stratigraphic

The type of oil trap attributed to each oil field in the state is indicated in table 2.

The classical and most widely known type of trap is the closed anticline. Indeed, most of the oil produced in California has been obtained from simple anticlines or from faulted anticlines. In the latter, faults commonly control the immediate localization of the oil within the folds. The next most common type of trap in California fields is the fault trap. Combinations of structural and stratigraphic traps are attributed to the remaining oil fields.

## COMPOSITION OF PETROLEUM

Petroleum is a mixture of naturally occurring hydrocarbons consisting of about 84-87 percent carbon and 11-13 percent hydrogen. Sulfur, nitrogen, and oxygen are the most abundant impurities. Although the elemental constitution of petroleum is simple and fairly uniform, the molecular construction is complex and varies widely. As many as 18 different series of hydrocarbons have been identified in crude petroleum, but hydrocarbons of only three series (paraffins, naphthenes, and benzenes) make up the greatest part.

The difficulties of classifying petroleum by the chemical constitution of the hydrocarbon compounds present have led to a simpler, less technical, two-fold classification. This is based on the character of the residue left by distilling away the lighter fractions in crude oil. *Paraffin-base* oils are those which leave a light-colored wax containing considerable amounts of hydrocarbons of the paraffin series. *Asphaltic-base* oils yield a dark asphaltic residue consisting predominantly of naphthene. An example of a typical paraffin-base oil is that produced in Pennsylvania. Most of the oil produced in California, Mexico, and the U.S.S.R. is of the asphaltic-base type.

## LOCALITIES

All of the producing oil fields in California are confined to the principal basins in which Tertiary sedimentary rocks were deposited. The major petroleum fields are grouped in the Los Angeles basin, Ventura basin, Santa Maria basin, San Joaquin basin, Cuyama basin, and the Salinas basin. Though crude oil production is negligible in northern California, the largest dry gas fields of the state are located there (see section on natural gas in this volume). Maps of the oil and gas fields, showing the location, ownership, and status of wells drilled can be purchased from the California Division of Oil and Gas, 205 Golden Gate Ave., San Francisco. An outline map of the state showing the boundaries of the available oil and gas field maps, and an index to fields, is published in the *Summary of Operations, California Oil Fields*, issued semi-annually by the Division of Oil and Gas.

## EARLY HISTORY OF EXPLORATION AND DISCOVERY

Drilling for oil in California began in the 1860's and was conducted mostly in the vicinity of oil seeps and outcrops of oil-impregnated rocks. With the development and application of surface and subsurface geologic methods of exploration, the discovery rate began to climb and many large and small fields were brought in. The discovery of such fields as Midway-Sunset (1910), Huntington Beach (1920), Elk Hills (1919), Signal Hill (1921), Santa Fe Springs (1921), Ventura Avenue (1925), and Kettleman Hills (1928) brought a prolific oil production and market expansion to California.

The development of the Midway-Sunset field led to the greatest gusher in the history of the United States' petroleum industry. This gusher, the famous Lakeview No. 1, flowed out of control for 544 days and reached an estimated peak daily output of approximately 68,000 barrels a few days after coming in. The discovery of deep zones in Ventura Avenue field proved a major addition to the state's reserves, and three pipelines were



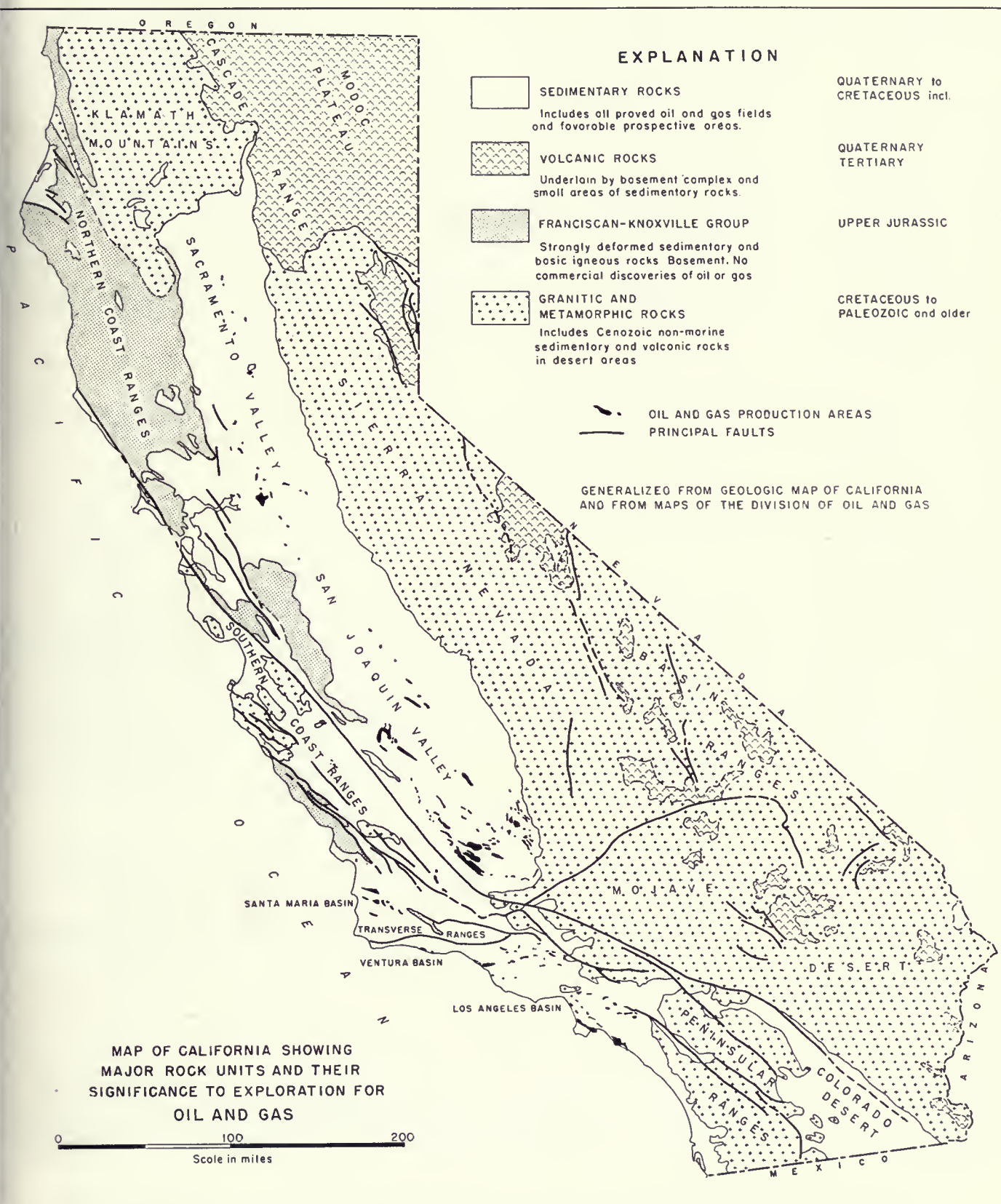


FIGURE 2. Map of California showing major rock units and their significance to exploration for oil and gas.



Table 2. Summary of geology and production of California oil fields.  
(Data from Division of Oil and Gas, Conservation Committee of California, Petroleum World, and Division of Mines Bull. 118 and Bull. 170.)

County	Field and areas	Year dis- covered	Type of accumu- lation <sup>1</sup>	A.P.L. gravity range	Average completion depths (feet)	Age of producing formations	Average number of producing wells July '54-Dec. '54		Oil produced during 1954 (bbl.)	Cumulative production to Jan. 1, 1955	Oil pro- duced per well per day (bbl.) July '54-Dec. '54	Proved acreage	
							Actual	Actual and potential				As of Dec. 31, 1954	Maxi- mum
Fresno	Burrel	1943	A	27°-31°	6606	Miocene	5	8	67,117	679,371	35.7	170	210
	Camden area	1951	F A	32°-34°	6098	Miocene	4	4	21,803	115,930	14.3	60	80
	Cantua Creek area (Turk Anti- cline)	1952	A	58°	9275	Eocene	2	2	4,395	37,216	7.1	20	20
	Chency Ranch area	1941	---	27°	7277	Cretaceous	0	1	0	12,459	0.0	10	10
	Coalinga	1896	A & S	12°-33°	1874-2935	Pliocene, Miocene, Eocene	1,648	2,018	7,114,312	477,151,258	11.6	17,421	18,594
	Coalinga, East, Extension	1938	A & S	25°-38°	8240-8215	Miocene and Eocene	150	229	16,695,008	288,326,192	320.3	4,060	4,550
	Guajarral Hills	1948	A & S	31°-40°	6200-8900	Miocene and Oligocene	81	94	2,667,874	20,684,455	109.0	1,550	1,660
	Helm	1941	A & F	30°-40°	6700-8100	Miocene, Eocene, and Cretaceous	74	100	891,879	14,803,594	34.9	4,000	4,545
	Jocalitos	1941	A & S	21°-40°	3800-4175	Miocene	106	123	590,156	16,382,035	14.8	2,440	2,590
	Pleasant Valley	1943	A & S	25°-30°	8900-9000	Eocene	21	25	471,813	11,401,213	61.2	420	500
	Raisin City	1941	A	24°-29°	5100-6300	Miocene and Eocene	111	125	1,943,701	16,224,420	52.2	1,295	1,370
	Riverdale	1941	A	33°-37°	6700-9000	Miocene and Eocene	41	53	612,080	12,556,838	39.3	1,020	1,630
	San Joaquin	1947	A	28°-30°	7030	Eocene	7	7	31,243	527,200	14.0	140	170
	Petrolia area	1953	---	55°	1600	Cretaceous	0	1	140	350	0.0	10	10
Humboldt	Ant Hill	1944	F A	13°-30°	3460-3660	Miocene	31	35	137,057	2,841,250	11.2	295	305
	Antelope Hills	1942	S & A	15°-30°	2244-2954	Miocene, Eocene	33	43	402,661	6,167,407	37.3	370	370
	Antelope Hills, North	1950	F A	15°-16°	2476	Miocene	12	22	246,874	1,617,407	36.8	235	235
	Bates area	1954	---	---	---	---	2	3	6,280	6,280	17.3	20	20
	Belgian Anticline	1946	F & A	28°-62°	3908-6872	Miocene, Oligocene, Eocene	81	110	3,107,642	11,012,112	106.4	935	945
	Bellevue	1944	F A	32°-36°	7532	Miocene	13	15	256,938	1,902,675	51.9	170	170
	Belridge, North	1915	A	15°-46°	7500-9000	Pleistocene-Pliocene-Miocene	72	150	598,645	61,032,494	23.1	1,885	1,915
	Belridge, South	1911	A & S	13°-30°	7500-4500	Oligocene	954	1,181	3,388,540	61,148,911	10.6	7,685	7,790
	Blackwells Corner	1941	FA & S	12°-15°	1216	Pleistocene-Pliocene; Miocene	25	31	29,940	500,660	3.2	200	200
	Calders Corner area	1949	S & A	37°-38°	8825	Miocene	2	2	25,000	216,976	31.3	30	50
	Canal	1937	A	39°	8550	Miocene	29	40	425,433	17,170,908	41.6	780	780
	Canfield Ranch	1938	A	26°-36°	7755-8127	Miocene	28	30	533,890	4,251,205	49.0	500	510
	Chico-Martinez area	1938	F	12°-14°	1040	Miocene	3	7	6,000	75,207	6.2	35	45
	Coles Levee, North	1938	A & S	32°-54°	9100-9900	Miocene and Eocene	142	159	5,391,262	78,565,433	107.0	3,530	3,530
	Coles Levee, South	1938	A & S	35°-37°	9700	Miocene	71	81	2,012,518	28,041,966	86.3	3,330	3,330
Kern	Comanche Point	1945	F?	13°-14°	620	Miocene	10	11	6,634	46,006	1.8	35	35
	Cymric	1916	A & S	11°-49°	1128-6523	Pleistocene, Pliocene, Miocene, Oligocene, Eocene	423	498	3,650,511	55,861,272	25.8	2,650	2,760
	Devils Den	1910	F & A	17°	1431	Pliocene	50	98	205,657	794,620	17.3	470	570
	Edison	1934	S & F	15°-29°	1680-4935	Pliocene-Miocene and basement complex	646	706	5,850,471	63,103,730	24.3	5,260	5,515
	Elk Hills	1919	A	21°-38°	3000-7750	Pliocene and Miocene	341	1,014	7,695,777	223,135,167	76.8	19,460	19,560
	Fruitvale	1928	S & F	16°-21°	4235	Pliocene and Miocene	339	412	3,580,703	62,610,562	28.6	2,690	2,785
	Greeley	1936	A & S	33°-38°	7790	Miocene	82	104	4,531,322	64,927,553	154.3	1,910	2,080
	Greenacres area	1953	S	19°-21°	11500	Miocene	2	2	6,390	7,599	6.7	10	10
	Jasmin	1946	---	19°-17°	4355-4690	Pliocene and Miocene	5	11	20,964	365,163	10.9	80	90
	Kern Bluff	1944	F A	14°-16°	1181	Miocene	129	133	443,044	3,653,105	9.4	555	565
	Kern Front	1925	S & F	13°-14°	2200	Pliocene and Miocene	677	728	2,248,232	84,343,862	8.8	4,270	4,295
	Kern River	1899	S & F	12°-14°	900	Pliocene	2,208	3,166	2,875,447	33,877,600	3.5	8,410	8,460
	Los Lobos	1952	A & S	15°-25°	6759-7526	Pliocene and Miocene	15	16	327,756	542,948	82.0	220	220
	Lost Hills	1910	A & S	15°-22°	1450-1700	Pleistocene, Pliocene, and Miocene	655	710	1,976,275	75,505,423	8.4	3,575	3,700
	Lost Hills, N. W. area	1953	---	27°	2740	Pliocene	4	4	8,053	11,701	10.2	40	40
	McDonald Anticline	1945	A	15°-41°	1550-2022	Miocene, Oligocene, Eocene	33	43	377,738	1,766,420	31.6	310	365
Kern	McKittrick	1898	F	11°-53°	1300-5000	Pleistocene, Pliocene, Miocene	241	303	936,538	100,251,470	10.8	1,115	1,245
	Midway-Sunset <sup>2</sup>	1900	S & A	12°-28°	1400-4800	Pleistocene, Pliocene, and Miocene	4,303	5,177	21,319,398	1,236,822,607	14.0	43,290	49,215
	Mount Poso	1927	F	13°-17°	1500-2500	Miocene	556	589	3,085,996	122,179,345	15.7	3,165	3,300
	Mountain View	1930	F	15°-30°	5140-6250	Miocene and basement complex	197	260	1,338,411	58,150,497	20.4	2,400	3,315
	Paloma	1939	A & S	34°-60°	19400	Miocene	123	159	2,652,237	45,577,260	57.2	6,030	6,420
	Pleito Creek	1951	A	13°-20°	11900	Miocene	14	15	152,560	400,145	28.8	170	170



Locality	Age	F & S	11°-15°	1250-2770	Pliocene and Miocene	291	332	1,325,015	20,691,366	11.8	2,285	2,360
Poso Creek	1932	F & S	11°-15°	11460	Pliocene	81	110	4,312,614	72,441,994	158.0	1,910	1,930
Rio Bravo	1937	A	38°-41°	5985	Miocene	19	19	527,937	1,257,740	74.3	190	225
Rosedale	1951	S & FA	26°-36°	4355	Miocene	25	30	503,684	881,816	74.8	450	450
Rosedale Ranch	1945	S	16°-21°	1635-2510	Pliocene and Miocene	375	405	1,793,333	68,258,398	13.2	2,390	2,440
Round Mountain	1927	F	13°-23°	8300-8530	Miocene	19	21	195,927	7,508,359	29.1	380	380
Strand	1939	A & S	34°-35°	2336-5732	Miocene	141	162	1,275,069	8,442,472	32.7	1,265	1,295
Tejon	1935	A & F	14°-40°	6919	Miocene	1	1	5,152	8,937	15.5	10	10
Tejon Flats area	1943	---	29°	6410-1888	Miocene and Oligocene	213	238	1,137,170	6,470,382	14.0	875	890
Tejon Hills	1958	F & S	25°-34°	503	Miocene	21	32	41,517	824,991	5.7	70	70
Tenblor Ranch	1900	FA	15°-16°	8500	Miocene	112	133	1,438,391	54,946,217	36.1	1,880	1,920
Ten Section	1936	A	36°-38°	5303	Miocene	3	4	32,395	854,042	33.3	80	50
Union Avenue	1941	F	15°	13000-	Miocene	3	4	32,395	854,042	33.3	80	50
Wasco	1938	A	30°-37°	15300	Miocene and Eocene	3	5	34,384	5,019,490	27.5	150	260
Welcome Valley	1952	S	11°-13°	2600-9750	Eocene	24	31	4,161	8,839	1.0	95	95
Wheeler Ridge	1922	A	21°-25°	7495-	Miocene, Oligocene and Eocene	88	92	1,863,988	8,691,313	63.0	605	655
Kettleman, Middle Dome	1931	A	49°	11588	Eocene	2	2	28,740	879,766	36.7	80	180
Kettleman, North Dome	1928	A	26°-53°	8296-	Miocene and Eocene	286	451	6,040,568	402,499,155	57.3	13,105	13,390
Pyramid Hills	1940	A & S	12°-40°	836-2957	Miocene, Oligocene, Eocene	35	40	99,796	935,299	10.1	290	290
Aliso Canyon	1938	FA	22°-53°	5300-7850	Pliocene, Miocene, Eocene	102	124	2,794,350	21,553,562	81.6	1,065	1,065
Alondra area	1946	A & S	27°-29°	9193	Miocene	5	5	77,206	1,348,197	40.0	50	50
Bandini area	1953	FA	40°-42°	5946	Pliocene	5	5	164,587	190,033	114.1	60	60
Beverly Hills	1908	A	17°-24°	2450-7100	Pliocene and Miocene	3	4	29,329	4,218,775	43.0	15	120
Castaic Hills	1951	FA	30°-36°	5978-6009	Miocene	53	56	1,218,178	3,800,481	55.1	485	485
Castaic Junction	1950	FA & S	20°-45°	10400-	Miocene	31	34	1,117,414	2,803,656	122.5	645	645
Del Valle	1940	FA & S	19°-68°	4747-	Pliocene and Miocene	82	87	1,072,200	18,033,545	37.0	630	640
Dominguez	1923	FA	26°-33°	4800-8000	Pliocene and Miocene	336	397	3,421,239	203,157,681	27.7	1,295	1,510
El Segundo	1935	A & S & Frc	20°-23°	7350-7450	Miocene and basement complex	15	17	75,075	12,633,683	14.3	220	773
Honor Rancho	1950	FA & S	30°-38°	4829-6384	Miocene	21	23	1,047,489	3,988,493	148.3	340	340
Horse Meadows area	1952	F	24°	4610	Cretaceous	1	1	7,459	23,435	19.8	10	10
Howard Townsite	1940	---	25°-60°	5725-8945	Pliocene and Miocene	26	26	202,989	2,462,572	20.7	165	195
Hyperion area	1944	A & Frc	16°-18°	6843	Miocene and basement complex	2	3	18,701	247,432	26.0	20	40
Inglewood	1924	FA	19°-33°	2300-8375	Pliocene and Miocene	471	491	4,658,033	194,825,131	27.7	975	988
La Mirada area	1945	F	35°	977	Miocene	1	1	3,980	25,250	0.4	--	20
Las Lajas area	1945	A	26°	5841-8068	Eocene	2	2	3,292	20,434	5.6	15	15
Lawndale	1928	A & S	20°-29°	9357	Pliocene, Miocene, basement complex	9	10	131,043	2,480,490	36.9	75	128
Leffingwell area	1946	F	30°-38°	4400-	Pliocene and Miocene	12	12	109,347	209,074	23.5	115	115
Long Beach	1921	FA	19°-29°	10600	Pliocene and Miocene	1,158	1,315	7,071,055	779,719,973	16.8	1,280	1,653
Long Beach Airport area	1954	F	33°	8500	Miocene	6	6	603,279	603,279	663.2	60	80
Los Angeles City	1892	F & A	12°-16°	894	Miocene	87	91	74,345	20,698,388	2.7	250	780
Los Angeles, East	1946	A	32°-35°	8582	Pliocene and Miocene	19	19	248,269	3,325,343	34.8	165	165
Mission area	1953	F	23°-29°	6195-7619	Miocene and Eocene	3	3	82,304	104,580	65.9	30	30
Montebello	1917	FA	29°-36°	3300-9000	Pliocene and Miocene	321	378	1,563,254	162,666,140	13.9	1,240	1,595
Newhall group	1875	---	13°-39°	893-3920	Pliocene and Miocene	45	120	116,670	6,395,902	7.3	405	660
Newhall-Potrero	1937	FA & S	33°-37°	6200-	Miocene	108	136	3,557,512	35,489,380	95.0	1,195	1,195
Oak Canyon	1941	A & S	22°-33°	10500	Miocene	20	20	418,920	6,802,116	56.5	270	270
Placentia	1949	F & S	12°-27°	2400-7200	Pliocene and Miocene	329	390	2,178,008	23,469,788	17.8	690	715
Playa del Rey	1929	A & S & Frc	21°-24°	1300-2000	Pliocene	98	136	505,613	55,609,964	14.5	465	590
Potrero	1928	A & F	23°-48°	4650-6300	Pliocene, Miocene, and basement complex	37	39	248,446	8,674,397	19.8	260	335
Rosecrans	1924	A & F	25°-60°	5143-	Pliocene and Miocene	168	197	975,779	64,680,020	16.1	580	708
Rosecrans, South	1939	A	27°-41°	4557-8946	Pliocene and Miocene	32	35	185,694	6,296,409	16.3	183	193
Salt Lake	1902	FA	12°-16°	6585-8216	Pliocene and Miocene	7	7	73,843	43,516,715	28.9	15	905
Sansinena	1940	FA	17°-33°	1960	Miocene	99	109	3,057,921	9,837,656	92.5	505	505
Santa Fe Springs	1921	A	29°-33°	2635-6880	Pliocene and Miocene	578	688	5,138,201	55,472,344	24.3	1,100	1,480
Seal Beach	1926	A & F	21°-34°	3500-8500	Pliocene and Miocene	234	250	3,542,690	138,020,171	41.8	620	690
Torrance	1922	A & S	12°-27°	4679-	Pliocene and Miocene	787	879	2,537,082	139,748,765	9.0	4,648	5,903
Turnbull	1941	FA	24°-28°	10086	Pliocene and Miocene	2	4	18,110	650,591	12.4	55	75
Walnut area	1948	F	16°-17°	3097	Miocene	4	5	4,904	22,834	6.9	40	40
Whittier	1898	F	12°-36°	1465	Pliocene and Miocene	137	201	493,020	23,385,559	13.0	615	733
Whittier Heights, North, area	1944	FA	15°-16°	2679-5129	Miocene	3	4	3,475	44,593	4.1	20	40
Wilmington	1936	FA & Frc & S	13°-32°	1638	Pliocene, Miocene, and basement complex	2,633	2,753	41,561,100	692,289,013	43.3	6,453	6,458

Kings

Los Angeles



Table 2. Summary of geology and production of California oil fields.—Continued.  
(Data from Division of Oil and Gas, Conservation Committee of California, Petroleum World, and Division of Mines Bull. 118 and Bull. 170.)

County	Field and areas	Year dis- covered	Type of accumu- lation <sup>1</sup>	A.P.I. gravity range	Average completion depths (feet)	Age of producing formations	Average number of producing wells July '54-Dec. '54		Oil produced during 1954 (bbl.)	Cumulative production of oil (bbl.) to Jan. 1, 1955	Oil pro- duced per well per producing day (bbl.) July '54-Dec. '54	Proved acreage	
							Actual	Actual and potential				As of Dec. 31, 1954	Maximum
Monterey	San Ardo.....	1947	A	10°-12°	2100-2500	Miocene.....	455	485	11,172,184	34,270,749	68.1	3,970	3,980
	Belmont Offshore area.....	1948	A	26°	8800	Miocene.....	2	2	13,932	75,305	45.4	30	30
	Brea-Ohnda.....	1889	F & A	19°-28°	2500-3900	Phocene and Miocene.....	570	732	8,347,734	237,865,441	39.6	2,275	2,418
	Coyote, East.....	1911	FA	19°-27°	3300-6400	Phocene and Miocene.....	263	284	2,402,173	70,876,556	24.7	1,235	1,410
	Coyote, West <sup>2</sup> .....	1909	A & S	13°-33°	4200-7000	Phocene and Miocene.....	331	353	2,678,816	181,407,336	21.9	1,010	1,053
	Huntington Beach.....	1920	A & F & S	13°-28°	2350-5000	Phocene and Miocene.....	1,496	1,722	21,617,904	545,600,300	40.7	5,035	5,300
	Kraemer.....	1918	A	18°-23°	2360	Miocene.....	19	23	76,858	2,153,551	12.8	75	140
	Newport.....	1947	F & S & Frc	9°-11°	1409	Miocene.....	0	6	1,250	171,501	0.0	30	175
	Newport, West.....	1922	A & F	12°-26°	1809-5445	Miocene.....	222	253	1,470,615	17,172,049	20.4	1,035	1,133
	Olive area.....	1933	FA & S	14°-15°	5545	Phocene.....	4	4	34,416	52,568	24.5	40	40
	Richfield.....	1919	A & S	17°-24°	3800-4200	Phocene and Miocene.....	408	442	2,738,796	125,881,763	18.0	1,445	1,530
	San Clemente area.....	1954	F	42°	4150	Cretaceous.....	1	1	1,452	1,452	4.2	10	10
	Sunset Beach area.....	1954	F	30°	6622	Miocene.....	2	2	35,590	35,590	106.2	60	60
	Talbert area.....	1947	F & S	19°	5626	Miocene.....	1	1	1,168	36,466	3.3	10	20
San Benito	Yorba Linda.....	1937	F & S	13°-20°	520-3156	Phocene.....	27	47	173,555	3,764,898	17.3	315	370
	Bitterwater area.....	1952	?	24°-25°	1629	Phocene.....	7	8	17,479	48,487	8.7	40	40
	Ciervo area.....	1948	A	15°-25°	1147	Eocene.....	4	6	4,922	27,310	5.2	20	20
	Lomeras area.....	1950	S & F	22°	2083	Phocene and pre-Eocene.....	1	1	0	5,909	0.0	20	20
San Bernardino	Vallecitos area.....	1944		36°	803-5312	Eocene, Cretaceous.....	0	2	937	5,383	2.7	10	10
	Chino-Souled area.....		FA			Miocene.....	8	9	20,451	64,898	8.0	30	30
	Arroyo Grande (Edna).....	1911	S	13°-21°	1265-2865	Miocene.....	23	48	40,803	1,822,315	5.1	330	610
	Guadalupe.....	1948	S	8°-14°	2798	Phocene and pre-Eocene.....	38	42	873,925	2,269,949	63.2	850	860
Santa Barbara	Morales.....	1950	S & F	28°-39°	2177-5908	Phocene, Miocene.....	25	28	175,057	1,325,853	22.3	210	220
	Taylor Canyon area.....	1950	S & F	31°-39°	5962	Miocene.....	2	2	38,240	223,673	49.8	20	20
	Barham Ranch area.....	1943	F	13°-15°	4831	Miocene.....	0	3	0	8,854	0.0	30	30
	Capitan.....	1929	FA	16°-43°	1400-2700	Miocene, Oligocene, Eocene.....	68	75	379,497	16,325,518	14.6	230	260
	Casmalia.....	1904	A	85°-11°	700-2800	Phocene, Miocene and Oligocene.....	63	92	683,040	17,749,522	30.3	1,090	1,700
	Cat Canyon group.....	1906	A	12°-26°	2400-6000	Phocene and Miocene.....	348	428	7,405,640	100,825,863	57.9	3,690	3,950
	Coal Oil Point area.....	1948	FA		10047	Miocene and Oligocene.....	0	1	1,279	1,279	0.0	10	10
	Cuyama, Central area.....	1951	S	43°	7372	Miocene.....	1	1	6,181	22,939	16.3	10	10
	Cuyama, South.....	1949	FA	26°-35°	4000-4500	Miocene.....	231	252	12,763,568	63,382,656	155.5	2,800	2,800
	Elwood.....	1928	A & Frc	32°-40°	3100-4400	Miocene and Oligocene.....	61	81	1,435,869	94,938,921	66.3	610	800
	Jesus Maria area.....	1952	A	14°	3571	Miocene.....	1	5	1,392	55,507	53.5	60	60
	Lompoc.....	1903	A	19°-21°	2200-2900	Phocene and Miocene.....	105	126	1,492,683	25,705,150	37.6	2,070	2,270
	Mesa (Santa Barbara).....	1929	F	17°-18°	1913	Miocene.....	4	6	5,395	3,656,972	3.9	6	200
	Orcutt.....	1903	A	18°-26°	1100-4280	Miocene and Miocene.....	265	329	1,265,647	116,088,957	13.4	3,650	4,680
Santa Clara	Russell Ranch <sup>3</sup> .....	1948	FA	21°-40°	3200-3700	Miocene, Phocene.....	160	178	3,999,006	37,212,972	67.1	1,320	1,320
	Santa Maria Valley.....	1934	S	12°-17°	2900-5500	Phocene, Miocene and pre-Tertiary.....	400	503	3,680,541	118,110,744	25.9	6,440	6,740
	Summerland.....	1887	FA	17°-19°	1228	Pleistocene and Phocene.....	1	9	3,585	3,212,836	11.1	90	260
	Zaca.....	1942	F	7°-8°	5000-5100	Miocene.....	42	43	1,708,887	8,730,361	110.2	460	460
Santa Clara	Moody Gulch.....	1880	F	40°-45°	980	Oligocene.....	1	2	468	64,925	12.2	20	80
	Sargent.....	1886	A & F	17°-18°	832	Phocene and Miocene.....	1	1	1,257	785,016	43.3	20	160



Sonoma	Petaluma area	1948	?	17°-20°	1061	Pliocene	1	2	352	11,606	1.8	50
Tulare	Deer Creek area	1941	S	17°	2305	Miocene	6	8	42,928	43,710	25.4	20
	Terra Bella area	1930	---	---	---	Miocene	0	3	170	24,999	---	45
Ventura	Bardsdale	1894	A	17°-37°	4199-6628	Oligocene and Eocene	94	119	440,051	6,279,854	12.9	410
	Conejo	1892	S	14°-16°	142	Miocene	6	10	358	108,955	1.8	20
	Fillmore area	1954	---	28°-29°	14313	Pliocene	2	2	129,832	129,832	364.4	20
	Montalvo, West	1947	A	13°-34°	9320-	Pliocene	18	20	439,437	2,027,284	77.9	480
	Oakridge	1952	A & S	16°-23°	12638	Pliocene, Oligocene, Eocene	39	41	1,002,960	2,415,874	76.0	400
	Ojai group	1885	---	11°-30°	2954	Miocene	81	133	233,063	4,906,150	7.5	845
	Oxnard	1937	S	6°-38°	844-4244	Miocene, Oligocene, Eocene	23	31	770,773	6,012,149	112.2	300
	Piru group	1882	A	16°-33°	2990-9707	Pliocene and Miocene	52	77	139,942	3,497,360	10.0	305
	Ramona <sup>4</sup>	1943	FA & S	14°-29°	225-5139	Pliocene	123	124	862,847	12,569,164	18.4	590
	Rincon	1927	FA	25°-31°	2379-4337	Pliocene	230	245	3,253,129	52,507,686	40.4	1,545
	San Miguelito	1931	FA	29°-34°	3500-6500	Pliocene	122	131	3,323,444	38,379,281	81.2	410
	Santa Paula group	1875	---	18°-36°	5500-8000	Pliocene	52	76	320,115	3,555,710	19.7	375
	Sespe group	1869	A & F	12°-34°	856-1976	Miocene, Oligocene, and Eocene	36	68	75,485	4,051,067	5.9	210
	Shiela Canyon	1911	A	20°-35°	2019-3466	Oligocene	161	185	379,840	15,819,322	6.3	910
	Simi	1912	FA & S	15°-43°	1250	Oligocene and Eocene	67	75	54,531	2,637,250	2.3	680
	South Mountain	1916	A	19°-30°	800-4500	Miocene and Eocene	374	380	5,420,355	51,699,806	40.9	2,220
	Tapo Canyon, South	1950	S & FA	17°-33°	542-2412	Miocene and Oligocene	18	24	752,403	1,637,933	138.3	220
	Temescal	1924	FA	21°-23°	2965	Miocene	21	21	145,699	4,959,435	18.8	150
	Torrey Canyon	1896	FA	19°-36°	1419-9832	Miocene and Eocene	67	76	1,301,802	8,461,899	55.5	230
	Ventura	1916	A & F	24°-32°	2400-	Pliocene	979	1,042	29,798,224	507,467,719	85.2	3,300

<sup>1</sup> A = anticlinal, F = fault, S = stratigraphic, Frc = fracturing.

<sup>2</sup> Includes part of Midway-Sunset field in San Luis Obispo County.

<sup>3</sup> Includes part of Kettleman, North Dome field in Fresno County.

<sup>4</sup> Includes part of Seal Beach field in Orange County.

<sup>5</sup> Includes part of Brea-Olinda field in Los Angeles County.

<sup>6</sup> Includes part of West Coyote field in Los Angeles County.

<sup>7</sup> Includes part of Russell Ranch field in San Luis Obispo County.

<sup>8</sup> Includes the portion of Ramona field in Los Angeles County.





FIGURE 3. Man-made island  $1\frac{1}{2}$  miles seaward from Seal Beach, constructed in water 42 feet deep. By September 1955 eight wells had been completed, and a ninth well was being drilled. Photo courtesy of Monterey Oil Co.

laid from this field to Los Angeles in 1925 and 1926. The development of the great Kettleman Hills oil and gas field led to the introduction of natural gas to the San Francisco Bay region in 1929.

A new era in the search for oil was introduced in the early 1930's with the application of the reflection seismograph to oil prospecting. The seismograph determined the existence of large anticlinal structures and thick sedimentary sections that had lain hidden deep beneath the alluvial fill of the San Joaquin Valley.

The Santa Maria Valley oil field, discovered in 1934, was the first major stratigraphic-trap oil field found in California after geologists recognized the importance of such features and began searching for them. This new approach to the search for oil yielded excellent results and accounted for the discovery of the East Coalinga Eocene field in 1938, the Antelope Hills field in 1942, the Cymric field in 1943, and the Gujarral Hills field in 1948.

The discovery of two new districts—Cuyama Valley and Salinas Valley—in 1948 made dramatic news, principally because they were wholly unexpected by most of the investigators in the oil industry. Within 2 years, these new districts added half a billion barrels to California's oil reserve and their ultimate yield should prove to be appreciably greater.

The existence of oil pools off California shores has been known for some time. As early as 1896, tideland wells were drilled at Summerland, Santa Barbara County. By 1906, the number of offshore wells along the beach and on piers at Summerland had reached 412. Oil beneath tide and submerged lands has since been

developed from coastal wells drilled at Rincon, Elwood, Capitan, Huntington Beach, Seal Beach, and Montalvo.

#### HIGHLIGHTS IN EXPLORATION 1952-55

During 1954, more exploratory wells were drilled for oil and gas in California than in any previous year. Of 632 exploratory wells drilled, 541 were dry holes and 91 accounted for new field discoveries, new extensions of previously producing pools, and deeper or shallower pools (Moody, 1955). The success factor for all exploratory wells drilled was 14.4 percent and new field wildcats had a success factor of 3.5 percent.

In late 1955, exploratory drilling was being carried on in every major sedimentary basin in the state and in the offshore waters along the coast. Deep drilling has become more common and has led to most of the new discoveries and most of the new oil reserves. From August 1953, to November 1955, California had the world's deepest well—Ohio Oil Company's "KCLA" 72-4 well in the Paloma oil field—which reached a depth of 21,482 feet. In December 1953, California also claimed the world's deepest producing well in the North Coles Levee oil field, Kern County, when Richfield Oil Corporation completed "C.L.A." 67-29 in the interval 17,497 to 17,792 feet.

In April 1952, the discovery of oil in Eocene beds at a depth of 9,600 to 9,756 feet in the Wheeler Ridge field proved the commercial possibilities of production from deep-lying Eocene beds. This opened a vast area in the San Joaquin basin to favorable consideration and prospecting. Data on significant new oil field discoveries and new oil pool discoveries that have been made during 1952-54 are listed in table 3.



Table 3. Oil fields and pools discovered in California during 1952-54, showing most notable production.\*

Year	New field or pool	Prod. depth of disc. well (feet)	Cumulative oil production to 12/31/54	No. of prod. wells 12/54	Production B/D, 12/54
1952	Deep Sespe pool in Torrey Canyon.....	9,327	2,208,826	14	3,103
	Eocene pool in Wheeler Ridge.....	9,756	2,012,075	16	4,035
	Oakridge field.....	3,300	2,415,874	39	2,696
	Antelope shale pool in Buena Vista Hills.....	4,400	2,754,977	38	3,815
1953	Terry pool in Tapo Canyon, South.....	2,507	1,655,329	17	2,221
	Alexander pool in Cat Canyon, West.....	3,650	1,390,290	25	1,407
1954	Leda, North pool in Guajarral Hills.....	8,940	1,138,836	24	4,846
	Long Beach airport.....	9,065	603,696	13	9,673
	Fillmore field.....	14,275	129,832	2	692
	Oleese pool in Tejon-Grapevine.....	5,744	246,974	15	2,349
	Exeter pool in Midway-Sunset.....	5,367	142,187	6	2,142

\*Data from Conservation Committee of California Oil Producers 1953-1955 and Am. Assoc. Petroleum Geologists Bull. June issues 1953-55.

Special mention should be given to the drilling program in the Twentieth Century Fox pool in the old Beverly Hills field which started in 1954 and was continuing into 1956. These wells lie in the heart of a residential section in greater Los Angeles. All operations are conducted under very stringent city ordinance requirements; the drilling rig is fully enclosed with soundproofing material, and electrical power is used throughout the well site. By late 1955, seven wells had been completed in this field and in November 1955, they were placed in production through pipe lines constructed during the war. Tremendous strides have been made by the oil industry in developing such techniques and equipment to eliminate unsightly and unpleasant features associated with oil fields.

In October 1954, the first California offshore well drilled from a man-made island, 75 feet in diameter, was completed off Seal Beach, Orange County. By September 1955, seven additional wells were drilled from the island and placed in production, and pipe-line facilities con-

necting the wells with the mainland were completed. Development of this offshore field is continuing and many additional wells are planned to be directionally drilled from this site.

At the end of 1955, a deeper fault block discovery in the Sunset Beach field appeared to be a most promising area. Several wells flowing 1000 to 2000 barrels per day were completed and in December more than 20 wells were drilling.

#### FUTURE EXPLORATION IN CALIFORNIA

A continuing search for additional fuel resources is indicated as an inevitable consequence of the future growth of California's population and industry. New reserves will be more difficult to find than in the past, but the search for them is being directed toward (1) discovery of offshore fields, (2) discovery of onshore fields in new areas, (3) extension of old fields, (4) discovery of new pools in known fields, and (5) improved methods of secondary recovery.



FIGURE 4. Piers in the sea follow extension of Rincon oil field seaward. Several deflected holes have been drilled from each derrick site on the piers. Offshore field is located about half way between Santa Barbara and Ventura.



*Tidelands Oil.* Mineral resources engineers of the State Land Commission have estimated that California's offshore oil deposits have a potential production of four billion barrels by primary recovery techniques (Hortig, 1954). In the future, offshore wells will be drilled primarily in the area of seaward extension of the Los Angeles basin where the Seal Beach offshore wells lie, as well as in the seaward extension of the Santa Barbara and Santa Maria basins. These seaward extensions are geologically part of the large sedimentary basins wherein lie three major oil provinces of the state. Other offshore potentialities are being studied from Humboldt Bay at the north to the Mexican border on the south.

During the 1955 legislative session, Governor Goodwin Knight signed into law a new tidelands oil bill which amends that part of the Public Resources Code relating to oil, gas, and mineral leases of state lands. Previously it had been necessary to show that offshore pools were threatened by drainage from onshore wells before the state could grant a tideland lease. This new law should provide the oil industry the long-awaited opportunity to explore for additional oil off the California coast.

*New Oil Areas.* Not only will new fields offshore be brought in but, in all probability, new fields in new areas onshore will be discovered. For example, the discovery of oil at Cuyama and San Ardo began the development of two previously undeveloped sedimentary basins. Today these fields are the sixth and seventh largest producing oil fields in the state. No big discoveries have been made in these two sedimentary basins since these fields were developed, but large areas of sedimentary rocks still remain untested by drilling.

Exploration beneath thrust faults may well lead to the discovery of hidden pools in some areas. Aliso Canyon oil field is a good example; here oil-barren Miocene rocks appear at the surface but drilling has revealed that these had been thrust over oil-bearing Pliocene rocks.

*Extensions of Old Fields.* The extension of presently producing fields should add considerable reserves in the future. As more and more development wells are drilled the subsurface geology becomes better understood and thereby information is provided showing where extensions to the fields lie.

*New Pools.* Discoveries of new pools in known fields will in all probability keep drilling activity at a high rate for years to come. Experience has shown that sometimes decades elapse after the discovery of a field before deeper zones are discovered. For example, the Buena Vista Hills field was discovered in 1909, but the 27-B pool was not discovered until 1944, the 23-B pool in 1950, and the Antelope Shale pool in 1952.

Until most fields have been drilled to basement rocks, the possibility of deeper production still exists. Modern technology has improved rotary drilling equipment to enable drillers to obtain depths over 20,000 feet. Although deeper drilling means higher costs, such wells are becoming more common.

*Secondary Recovery.* In secondary recovery lies one of the greatest potential oil reserves. The presently non-recoverable oil contained in all known California oil fields probably exceeds all of the state's past production or more than 10 billion barrels of oil. A portion of this

residual crude will become available as methods of extracting it are perfected. Water flooding and gas injection already have become important phases of production in many California fields. Basically, water flooding consists of injecting water into the oil reservoir through intake wells located on the margin of the field in order to drive or flush the oil toward producing wells. In the gas injection method of secondary recovery, the gas which is injected under pressure transmits the pressure to the oil and a pressure gradient is established from the intake well to the producing well (Levorsen, 1954, p. 463). In addition, the gas dissolves in the oil, lowers its viscosity, and permits it to flow more freely through the reservoir.

In 1955, several fields were undergoing experimental secondary recovery projects. For example, in the San Miguelito field water was pumped directly from the ocean to an elevation of about 1000 feet and then injected into the Third Grubb pool located about 8,000 feet below sea level. This marked the first use in California of water taken directly from the sea. Another example is in the Dominguez oil field where one of the largest water floods in a California field was started in July 1954.

In several California oil fields the recovery of highly viscous crude oil is undertaken by introduction of diluents, heating elements, hot water or steam. At the San Ardo field, for example, oil of 10° to 12° gravity blended with warm higher gravity oil to produce about 30,000 barrels of 14.5° gravity oil per day. In 1955, a new experiment in secondary recovery by in situ combustion process was started in the South Belridge field. Fundamentally, this method consists of setting an underground fire whereby the heat will reduce the viscosity of the oil and drive the hydrocarbons toward producing wells. This test will be the first attempt in California to recover heavy oil from a commercial field by means of an underground combustion process. The experiment, which is expected to take 2½ to 3 years to complete and to cost about \$1,000,000, was planned to determine if thermal recovery is feasible from both engineering and economic points of view. Another pilot-scale field test of a secondary recovery method involving combustion of underground formations is being planned for an area in the Midway-Sunset field. The objective of the test will be to determine if this method of secondary recovery outperforms water and gas injection methods on certain types of structures and crude oils.

## PRODUCTION

California's oil industry has undergone remarkable changes in the past decade. Before World War II, production of crude oil in California fields was far in excess of local demand, and large quantities of crude oil and gasoline often were sold on the world's markets for whatever prices they would bring. Since World War II the demand for petroleum caused by the greatly increased population and the rapid industrialization of many parts of the state has surpassed the productive capacity of the local refineries. Since 1951 the refineries in California have imported substantial quantities of crude from foreign sources. Exports of oil, however, have continued to be large, so that at the present time California refineries simultaneously import and export crude oil. This seeming paradox is attributable mostly



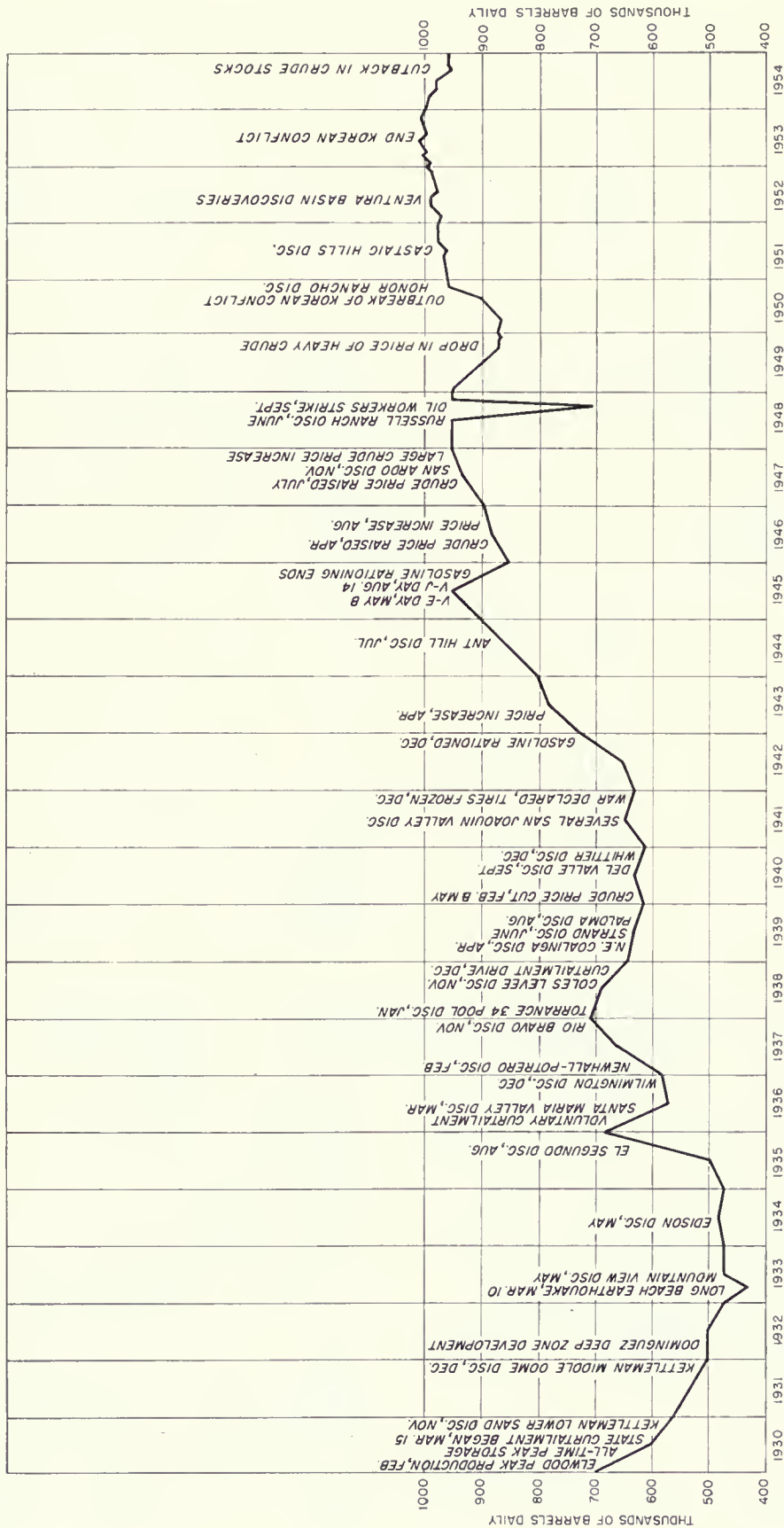


FIGURE 5. Chart showing crude oil production 1930-54, and historical events that influenced production.



Table 4. Six largest crude petroleum producing states 1949-53.\*

State	Production in thousands of barrels					Percent of total crude oil produced in U. S. in 1953
	1949	1950	1951	1952	1953	
1. Texas.....	744,834	829,874	1,010,270	1,022,139	1,019,164	43.4
2. CALIFORNIA.....	332,942	327,607	354,561	359,450	365,085	15.5
3. Louisiana.....	190,826	208,965	232,281	243,929	256,632	10.8
4. Oklahoma.....	151,660	164,599	189,869	190,435	202,570	8.6
5. Kansas.....	101,868	107,586	114,522	114,807	114,566	4.9
6. Wyoming.....	47,890	61,631	68,929	68,074	82,618	3.6

\* From U. S. Bur. Mines Minerals Yearbook, 1953.

the high proportion of low gravity crude oils produced in California, which are difficult and costly to refine. As a result, residual fuel oil inventories were becoming burdensome in 1953 and 1954 while demand for refined products was increasing. In 1955, however, the output of this less valuable residual oil was reduced as refineries were modernized to increase the output of gasoline and other higher valued products.

Table 5. Twelve California fields of largest production during 1954.\*

	Average number producing wells	Production in 1954 (thousands of barrels)
1. Wilmington.....	2,633	41,561
2. Ventura.....	979	29,798
3. Huntington Beach.....	1,496	21,618
4. Midway-Sunset (including Buena Vista).....	4,303	21,319
5. Coalinga, East, Extension.....	150	16,695
6. Cuyama, South.....	231	12,764
7. San Ardo.....	455	11,172
8. Brea-Olinda.....	570	8,348
9. Elk Hills.....	341	7,696
10. Cat Canyon.....	348	7,406
11. Coalinga.....	1,648	7,114
12. Long Beach.....	1,158	7,071

\* California Div. Oil and Gas statistics.

California crude oil production reached an all-time high in 1953 when it exceeded one million barrels per day or a total of 367,292,000 barrels for the entire year (California Division of Oil and Gas, 1953-55). During 1954, production dropped to 357,704,000 barrels. Approximately 15,000 barrels per day of heavy crude production was shut-in in California during 1954 when residual fuel oil inventories were becoming high. In the latter part of 1955, the trend of production began to head upward again as shut-in fields were reinstated. By December 31, 1954, oil was being produced in California from an average of 32,492 producing wells located in approximately 175 oil fields (California Division of Oil and Gas, 1954). To the end of 1954, the cumulative production of crude oil in California amounted to 10,108,493,356 barrels. California ranks second to Texas in crude-oil productive capacity, and provides about 15 percent of the nation's oil.

#### PRICES

The average value of California crude petroleum at the well as calculated by the U. S. Bureau of Mines (White and Coumbe, 1953), rose from \$2.23 per barrel in 1952 to \$2.49 per barrel in 1953, and the total value

of crude produced increased from \$801,570,000 to \$909,060,000. The increase in total value was the result of increased production and higher prices per barrel. No changes in price paid for crude oil were made during 1954, but new price adjustments were made on October 17, 1955. According to the Standard Oil Company of California Schedule No. 132, October 1955, California crude oil prices per barrel (42 U. S. gallons) at the well ranged from \$1.52 for 12 gravity oil to \$3.49 for 41 gravity oil.

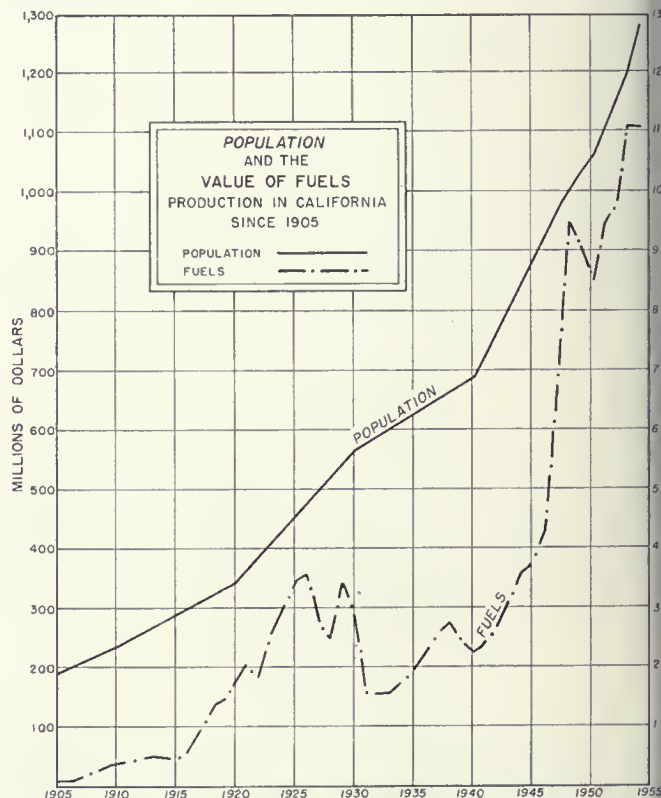


FIGURE 6. Population and the value of fuels production in California since 1905.

#### RESERVES

The Committee on Petroleum Reserves of the American Petroleum Institute estimated the proved reserves of crude oil in the United States on December 31, 1953 to be 29 billion barrels. These estimates include only oil recoverable under existing economic and operational conditions. As of December 31, 1953, Texas had 52 percent of the total estimated reserves, California 13 per



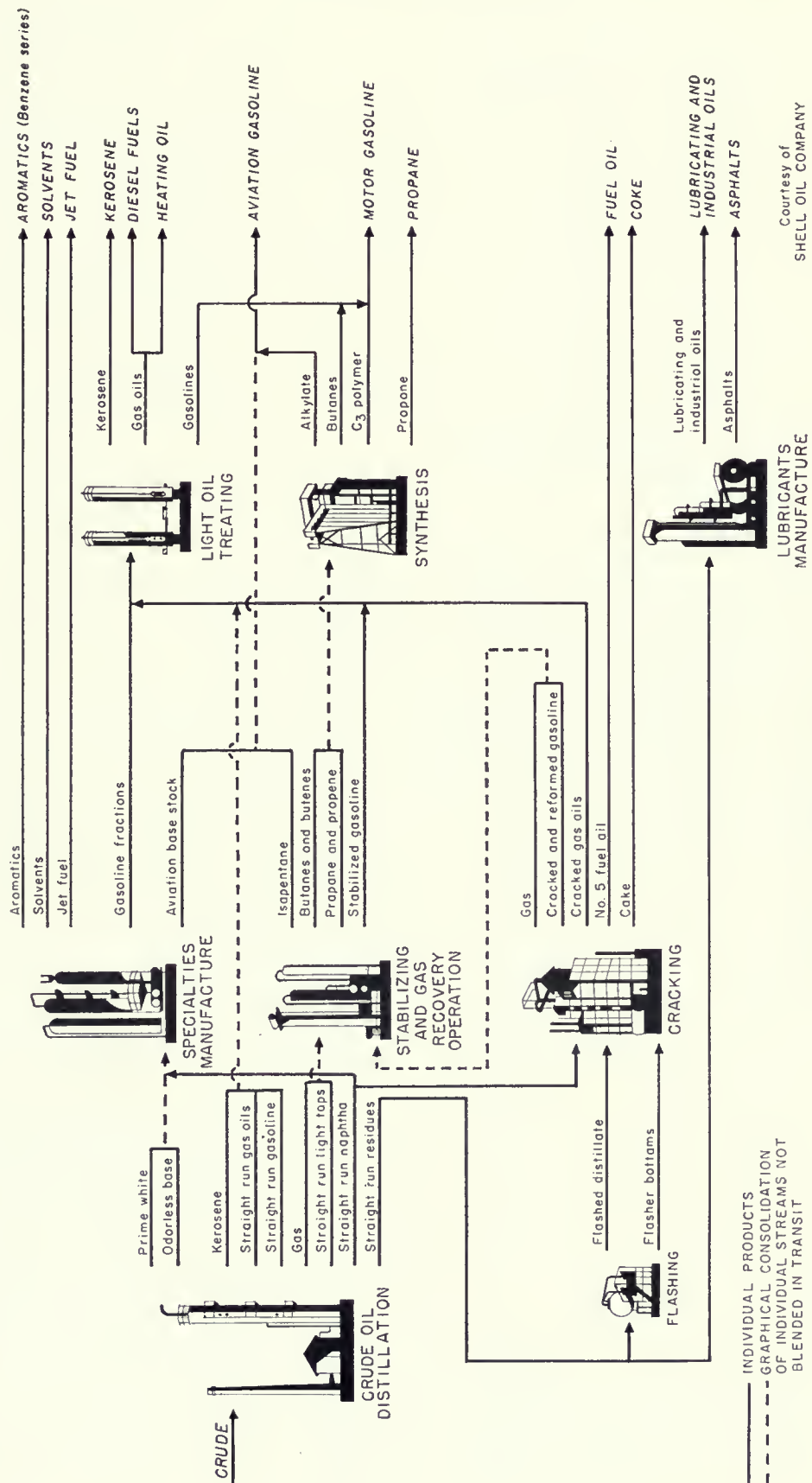


FIGURE 7. Simplified flow diagram of an oil refinery.



cent, Louisiana 10 percent, and Oklahoma 6 percent, or 81 percent for the four states combined. The 33 major oil fields in California (fields from which ultimate production is expected to reach at least 100 million barrels) account for approximately four-fifths of all the crude both discovered and produced to date in California (Moody, 1954).

Table 6. *Estimated petroleum reserves (millions of barrels) in six leading states on December 31, 1949-53.\**

State	1949	1950	1951	1952	1953
1. Texas.....	13,510	13,582	15,315	14,916	14,999
2. CALIFORNIA.....	3,823	3,734	3,761	3,854	3,920
3. Louisiana.....	1,910	2,185	2,285	2,558	2,760
4. Oklahoma.....	1,330	1,397	1,476	1,558	1,752
5. Wyoming.....	692	841	973	1,065	1,279
6. Kansas.....	738	732	792	917	913

\* From U. S. Bur. Mines Minerals Yearbook, 1953. Table indicates amount of crude oil that may be extracted by present methods from fields completely developed or sufficiently explored to permit reasonably accurate calculations. The change in reserves during any year represents total new discoveries, extensions, and revisions, minus production. Excludes condensate.

### UTILIZATION

Crude oil is converted into a vast number of finished products at refineries before sale to ultimate consumers. The primary use of petroleum is to produce energy for power or heat, and for lubricants. The products of refining and their chief uses are shown in table 8. Other miscellaneous products supplied by the petroleum industry represent only a small percentage of the crude oil produced, however, they are a vital factor in the national economy. Most significant among these are raw materials

Table 7. *Input and output of petroleum products at refineries in California, during 1953, in thousands of barrels.<sup>1</sup>*

<b>Input:</b>		
Crude petroleum.....		381,954
Natural-gas liquids.....		27,599
Total input.....		409,553
<b>Output:</b>		
Gasoline.....		162,926
Residual fuel oil.....		134,784
Distillate fuel oil.....		55,821
Still gas <sup>2</sup> .....		13,869
Asphalt <sup>3</sup> .....		11,256
Jet fuel.....		5,012
LP—gases.....		4,828
Lubricating oil.....		4,614
Road oil.....		2,544
Coke <sup>4</sup> .....		2,185
Kerosene.....		2,060
Wax <sup>5</sup> .....		342
Other miscellaneous.....		1,926
Other unfinished oils (net).....		9,078
Overage.....		1,692
Total output.....		409,553

<sup>1</sup> Preliminary figures; from U. S. Bur. Mines Minerals Yearbook, 1953.

<sup>2</sup> 3,600 cu. ft. still gas = 1 bbl.

<sup>3</sup> 5.5 bbls. asphalt = 1 short ton.

<sup>4</sup> 5.0 bbls. coke = 1 short ton.

<sup>5</sup> 280 pounds wax = 1 bbl.

for fertilizer and rubber industries. Sulfur from natural gas and refinery gas and ammonia from petroleum helped to increase the nation's fertilizer supplies. Most of the raw material for the synthetic rubber industry came from petroleum refineries and petrochemical plants. Petrochemical products from both crude and natural gas include: chemicals, solvents, plastics, synthetic fibers,

Table 8. *Petroleum products and their uses.*

Products	Uses
Gasoline.....	Motor fuel (highway and aviation).
Residual fuel oil.....	Heavy fuel for vessels, gas and electric companies, heating, oil companies, military, railroads.
Distillate fuel oil.....	Heating, diesel locomotive fuel, diesel trucks.
Kerosene.....	Range oil (cooking, water heating, small space heating) tractor fuel, lighting.
Jet fuel.....	Military aviation.
Lubricating oil and grease.....	Automotive and industrial purposes.
Wax.....	Waterproofing containers and paper, candles.
Coke.....	Carbon anodes for electrolytic refining of aluminum, refinery fuel, domestic furnace fuel, graphite electrodes, abrasives, carbide manufacture.
Asphalt.....	Road paving, roofing material, waterproofing, pipe coatings, moldings, paints, lacquers, blending with rubber, briquetting.
Road oil.....	Roads.
Still gas.....	Refinery fuel.
LP—gases.....	Domestic and commercial heating, chemical uses, motor fuel, synthetic rubber manufacture, industrial fuel.

drugs, detergents, resins, dyes, explosives, saccharine, carbon black, antiseptics and perfumes.

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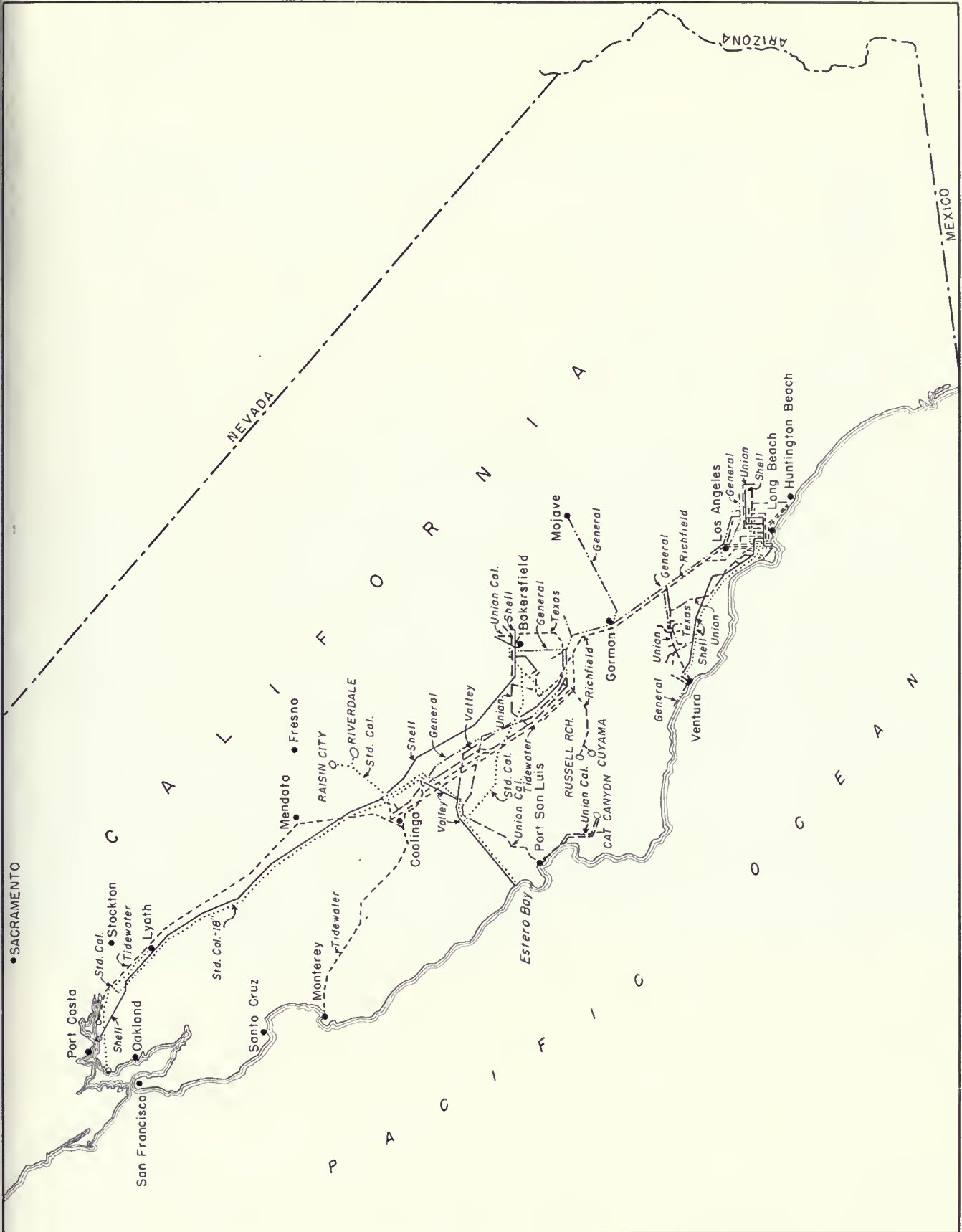


FIGURE 8. Crude oil pipelines. Modified from Oil and Gas Journal, vol. 54, no. 23, 1955.



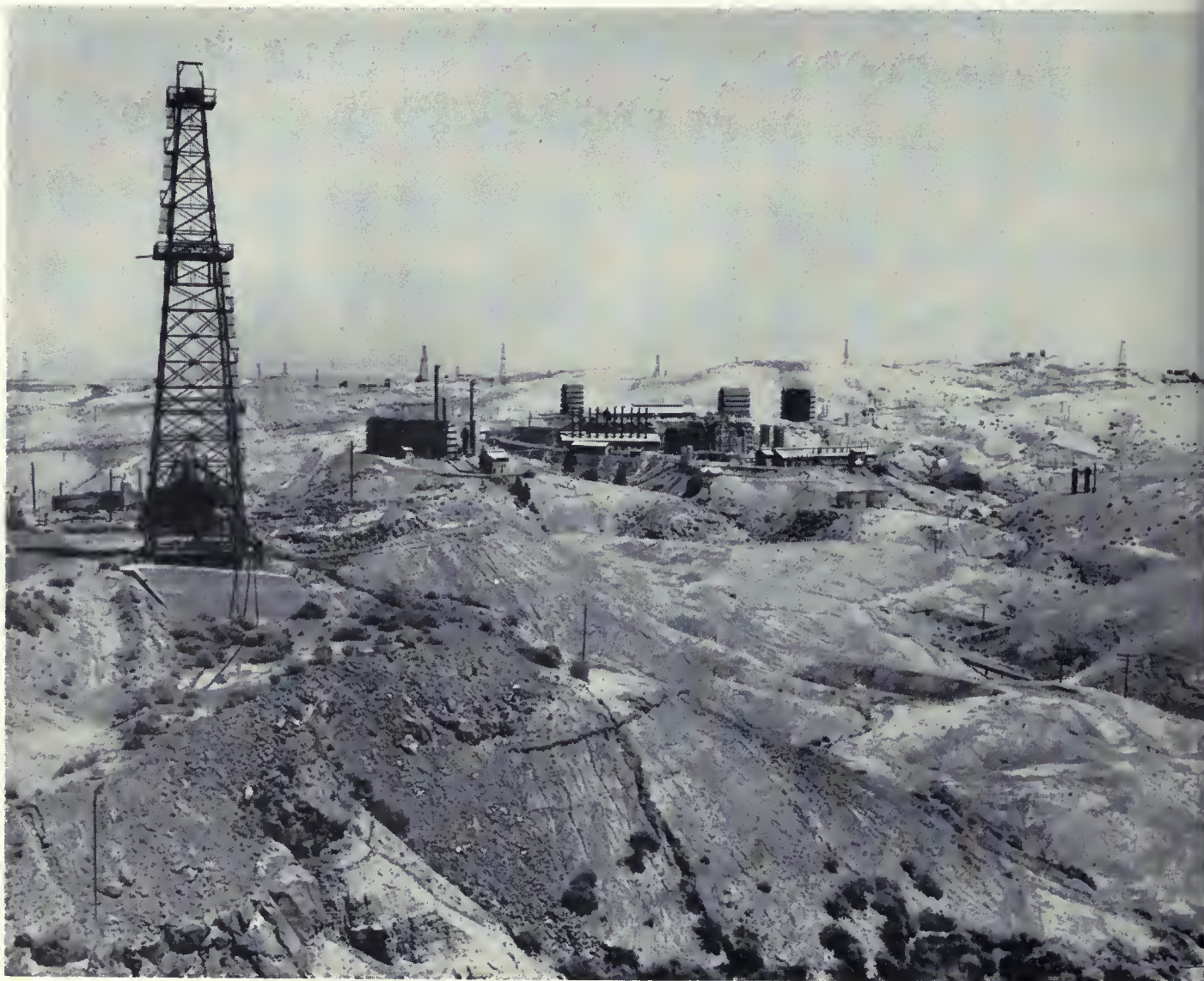


FIGURE 9. View southeast toward Kettleman Hills North Dome, Kings County. *Reprinted from California Journal of Mines and Geology, vol. 49, pl. 6.*



By CHARLES J. KUNDERT

## GEOLOGIC OCCURRENCE

Under humid weathering conditions, calcium carbonate is removed in solution from low-grade phosphatic limestones, and residual deposits of phosphate rock accumulate. The Florida deposits, from which about three-

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graph TD
    EP((ELEMENTAL PHOSPHORUS)) --> MU((MILITARY USES))
    EP --> PC((PHOSPHORIC ACID))
    EP --> POC((PHOSPHORUS OXIDE))
    EP --> ZP((ZINC PHOSPHIDE))
    EP --> PS((PHOSPHORUS SULFIDE))
    EP --> PCH((PHOSPHORUS CHLORIDE))
    EP --> RPP((RED PHOSPHORUS))

    MU --> IB[Incendiaries]
    MU --> SS[Smoke Screens]
    MU --> TB[Tracer Bullets]

    POC --> LA[Dehydrating Agent]

    ZP --> M[Matches]
    ZP --> L[Lubricants]

    PS --> L

    PCH --> O[Organic Synthesis]
    PCH --> I[Insecticides]
    PCH --> P[Plasticizers]

    RPP --> M

    PC --> CPH((CALCIUM PHOSPHATE))
    PC --> APH((AMMONIUM PHOSPHATE))
    PC --> SPH((SODIUM PHOSPHATE))

    CPH --> SC[Leavening Agents]
    CPH --> SF[Stalk Feed]
    CPH --> CC[Calcium Conditioner]
    CPH --> D[Deinfricatives]
    CPH --> P[Paper]
    CPH --> F1[Fertilizer]
    CPH --> SO[Soft Drinks]
    CPH --> MC[Metal Coatings]

    APH --> FR[Fire Retardants]
    APH --> YC[Yeast Culture]
    APH --> F2[Fertilizer]

    SPH --> P1[Photography]
    SPH --> PH[Pharmaceuticals]
    SPH --> O1[Ostergents]
    SPH --> LA1[Leavening Agents]
    SPH --> W[Water Conditioning]
    SPH --> SW[Silk Weaving]
    SPH --> SB[Soap Builders]
  
```

The phosphate shale member of the Permian Phosphoria formation contains the mineable phosphate beds. It is about 75 to 150 feet thick, and consists of yellow to brown phosphatic sandstones, dark brown to black phosphatic shales, brown to black limestone beds and



one to three beds of gray, brown oölitic phosphate rock. The richest beds of phosphate rock range from 3 to 7 feet in thickness and contain from 26 to 36 percent  $P_2O_5$  (Ruhlman, 1955, p. 3).

Being a true bedded sedimentary deposit analogous to coal, the Phosphoria formation is of uniform thickness and quality over wide areas (Mansfield, 1927, p. 214). It has been widely exploited by both surface and underground mining methods in Idaho, Montana, Utah, and Wyoming. In 1954, about 900,000 long tons of phosphate rock were yielded by mines in Idaho, and about 700,000 long tons were yielded by mines in Montana, Utah and Wyoming (Ruhlman, 1955, p. 3). Most of the mined rock is of commercial grade. However, two companies in 1954 were beneficiating part of their phosphate rock production (Ruhlman, 1955, p. 4).

In 1953, the following companies were producing phosphate rock from the western phosphate field (Ruhlman, E. Robert, 1955, p. 7):

Company	Location of mines	Type of mine	
		Underground	Open pit
Anaconda Copper Mining Company	Conda, Idaho	x	x
Garfield Chemical & Mfg. Co.	Thistle, Utah		x
Monsanto Chemical Company	Soda Springs, Idaho		x
Montana Phosphate Products Company	Garrison, Montana	x	
George Relyea	Garrison, Montana	x	
San Francisco Chemical Company	Montpelier, Idaho	x	x
	Leele, Wyoming	x	
	Woodruff, Utah		x
J. R. Simplot Co.	Fort Hall, Idaho		x
	Randolph, Utah		x
Victor Chemical Works	Melrose, Montana		x

#### LOCALITIES IN CALIFORNIA

Phosphates have not been recovered on a commercial basis in California, and no deposits of proved commercial value have been discovered. At some localities, notably in the western San Gabriel Mountains, igneous rocks are unusually rich in apatite. A computed average of five titanomagnetite rocks from the San Gabriel Mountains showed a composition containing six percent apatite (Oakeshott, 1949, p. 1942). Nodules and pellets of collophane are found in the Cenozoic marine sedimentary rocks of California. The presence of these nodules, together with the fact that phosphatic nodules have continued to form off the coast of California, suggest that commercial deposits may be found in the Cenozoic marine sedimentary rocks of the state.

At Carmel Valley, Monterey County (Rogers, 1944), phosphate-bearing strata occur as two poorly defined beds in Miocene shale. These beds, about half a mile apart, range from 6 inches to 1 foot in thickness, and are composed of pellets which are possibly micro-coprolites.

In the Palos Verdes Hills phosphatic shale and nodules occur in the Altamira shale, Valmonte diatomite, and Malaga mudstone members of the Monterey formation. Phosphatic shale is the characteristic lithologic type of the upper Altamira shale member. Limy phosphatic nodules, presumably derived from the Monterey

formation, are present in the lower Pleistocene Lomita marl (Woodring, Bramlette, and Kew, 1946, pp. 16, 34, 37, 50).

Collophane oölites or pellets occur in the Miocene sedimentary rocks of the state, particularly in the Monterey formation. They have been used for correlation purposes by petroleum geologists. Collophane pellets have been reported from the southern San Joaquin Valley (Galliher, 1931, p. 258), Los Angeles and Orange Counties (Emery and Dietz, 1950, pp. 11-12), Santa Barbara and Monterey Counties (Galliher, 1931, p. 266), and San Luis Obispo County (Rogers, 1944, p. 419). A small deposit of phosphate rock was found in Pleistocene sediments near Big Pine, Inyo County (Tucker, 1926, p. 520), and minor occurrences have been noted in San Diego (Merrill, 1916, p. 717) and Ventura Counties (Tucker, 1925, p. 242).

#### UTILIZATION AND MARKETS

A small amount of phosphorus is essential to the normal growth of most plants. Because many soils are lacking phosphorus, or contain "fixed" phosphorus compounds unavailable to plants, phosphatic fertilizers are added to the soil. Recorded historical use of phosphatic materials as fertilizers dates back to about 200 years B.C. In 1954, about 60 percent of the domestic production of approximately 14 million long tons of phosphate rock was used in agricultural fertilizers. About 25 percent was used in making elemental phosphorus and phosphoric acid from which organic and inorganic chemicals are derived. These chemicals are utilized in leavening agents, water softening products, soaps and detergents, plasticizers, and insecticides and other uses. Elemental phosphorus is used in making military smoke screen bombs and shells, incendiary bombs, pesticides, and phosphorus alloys. Phosphoric acid is used in the production of fertilizers, stock and poultry feed, beverages, ceramics, as a catalyst and oil refining agent, in photography, and in dental and silicate cements. It has been used as a substitute for sulfuric acid in certain industrial processes. The remaining 15 percent of domestic production of phosphorus rock was exported, largely for use in fertilizers.

In 1954 about eight hundred thousand tons of commercial fertilizers were consumed in California. Most commercial fertilizers contain some form of phosphate. Ground phosphate rock is sometimes added directly to the soil, but because it is relatively insoluble, the beneficial effects are not immediately apparent. Therefore, phosphate rock is usually converted to water-soluble calcium acid phosphate ( $CaH_4P_2O_4$ ) before it is compounded into fertilizer.

The following descriptions of three methods of processing phosphate rock to obtain products suitable for fertilizer and industrial purposes are quoted from Ruhlman (1955, pp. 6-8):

"1. In the acid treatment, phosphate rock is mixed with sulfuric, phosphoric, or nitric acid or a combination of the three.

Decomposing phosphate rock with sulfuric acid produces either ordinary super phosphate or phosphoric acid. When ordinary super phosphate is wanted, enough sulphuric acid is added to high-grade phosphate rock to convert the phosphate into water-soluble or available monocalcium phosphate. Calcium sulfate is also produced but is not separated from the mixture, which seldom contains over 20 percent available  $P_2O_5$ . To produce phosphoric acid,



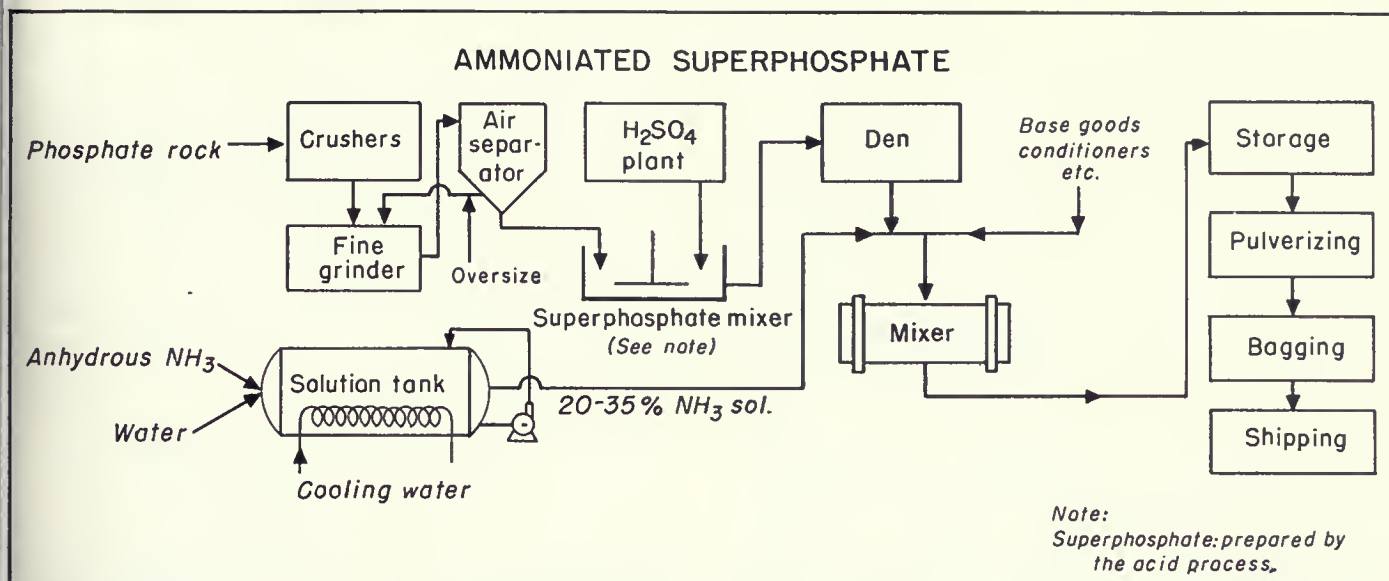


FIGURE 2. Flow sheet showing production of ammoniated superphosphate by the acid process. Modified after Olive and Shreve (1947). Published by permission of McGraw-Hill Book Co., Inc.

additional sulfuric acid is added, and the phosphoric acid is filtered from the insoluble calcium sulfate.

"Acidulating phosphate rock with phosphoric acid produces triple superphosphate. Also, phosphoric acid may be combined with potash and/or ammonia to produce highly concentrated fertilizer salts, such as ammonium phosphates and potassium phosphates. . . .

"Using nitric acid or a combination of nitric and another acid for acidulation of phosphate rock has not been used extensively in the United States. The resulting product, because of the hygroscopic calcium nitrate content, must be further treated, usually by ammoniation to produce a suitable fertilizer product. Further use of nitric acid processes will depend on the availability and cost of nitric and sulfuric acids.

"2. The thermal reduction method is based on the smelting of phosphate rock with carbon (coke) and a siliceous flux in electric or blast furnaces. The products are elemental phosphorus, ferrophosphorus, carbon monoxide, and calcium silicate. The phosphorus is volatilized, condensed, and collected under water as a heavy liquid. The calcium silicate is tapped from the furnace as a molten slag. Small quantities of ferrophosphorus, produced from the iron in the phosphate rock, are tapped from the furnace and marketed as a byproduct.

"Phosphoric acid is produced by burning phosphorus and hydrating the  $P_2O_5$  produced. The phosphoric acid may be converted into various fertilizer or industrial phosphorus compounds. Calcium metaphosphate is produced by burning elemental phosphorus in a chamber into which pulverized phosphate rock is blown. The phosphate rock and  $P_2O_5$  react to yield molten calcium metaphosphate, which is tapped and cooled to form a glassy solid.

"3. There are three variations of thermal treatment without reduction. These are: (a) Heating phosphate rock with an alkali salt (for example  $Na_2CO_3$ ) with or without substantial defluorination; (b) heating phosphate rock in the presence of water vapor to defluorinate the rock as completely as possible; and (c) fusion of phosphate rock mixed with magnesium silicate (serpentine or olivine). Following grinding these products do not receive further treatment. . . ."

In 1955 four concerns in California were using the acid treatment method to produce phosphatic products. The Best Fertilizer Company at Lathrop acidulates phosphate rock to produce phosphoric acid, ammonium phosphate and other mixed fertilizers. The Chemurgic Corporation at Fresno produces mixed fertilizers from

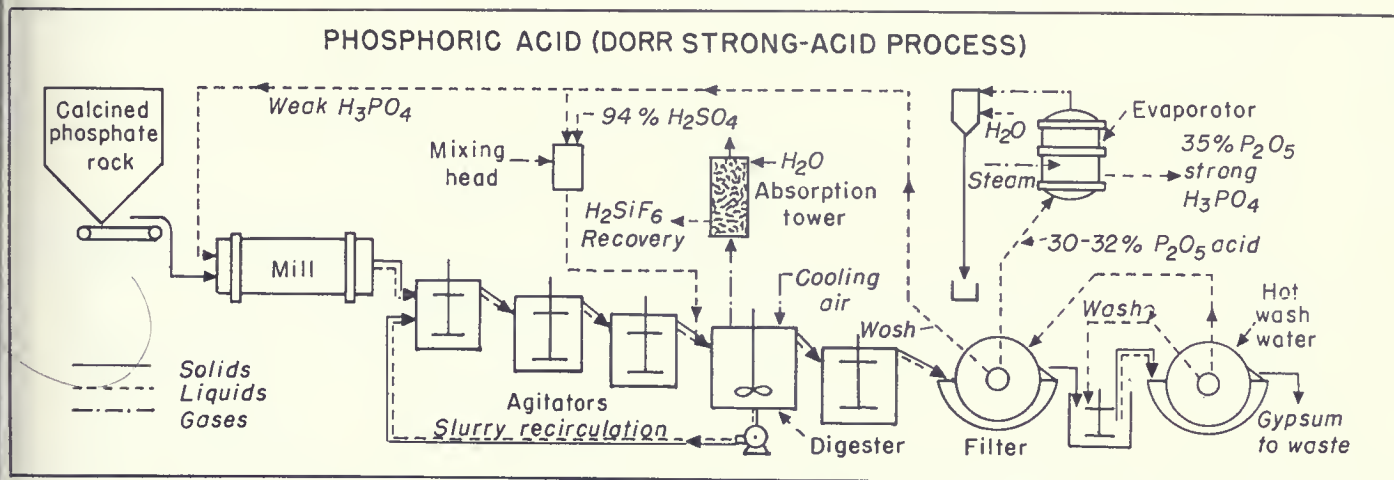


FIGURE 3. Flow sheet showing production of phosphoric acid by the Dorr strong-acid process. Modified after Olive and Shreve (1947). Published by permission of McGraw-Hill Book Co., Inc.



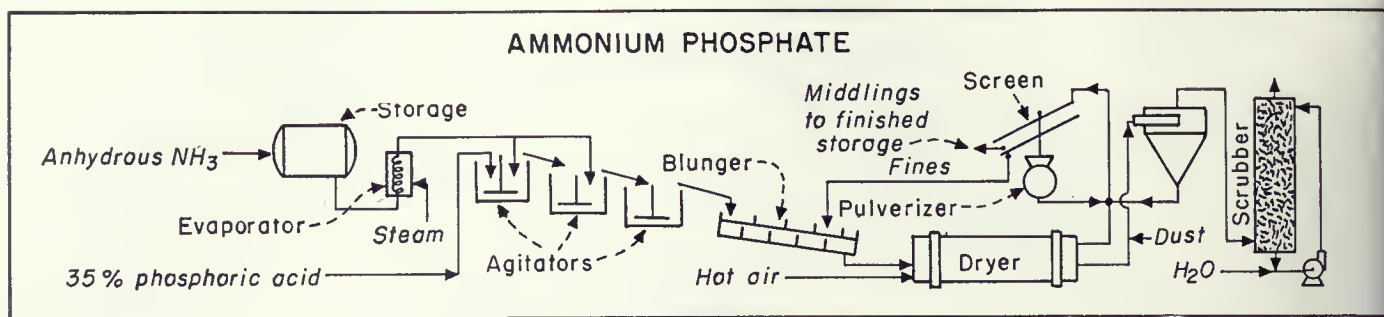


FIGURE 4. Flow sheet showing production of ammonium phosphate from ammonia and phosphoric acid. Modified after Olive and Shreve (1947). Published by permission of McGraw-Hill Book Co., Inc.

acidulated phosphate rock. Stauffer Chemical Corporation operates plants at Richmond and Vernon which manufacture water soluble phosphate (superphosphate). Western States Chemical Corporation at Nichols acidulates phosphate rock to produce phosphoric acid as well as ammonium phosphate and other mixed fertilizers. In the past Mountain Copper Company, Ltd., made superphosphate at its plant in Martinez.

In 1955, two California concerns were making phosphate products from elemental phosphorus produced by the thermal reduction method. One of these, the Westvaco Chemical Division of Food Machinery and Chemical

Corporation at Newark, was producing phosphate chemicals, principally complex sodium phosphates, from elemental phosphorus which had been produced by an electric furnace at its plant in Pocatello, Idaho. The Monsanto Chemical Company at Long Beach, in 1955, was producing phosphate chemicals and fertilizers from elemental phosphorus. The elemental phosphorus is shipped from Soda Springs, Idaho, where it is made by the electric furnace method from low-grade phosphatic shale.

The thermal treatment without reduction method was used in the late 1940's by Permanente Metals Cor-

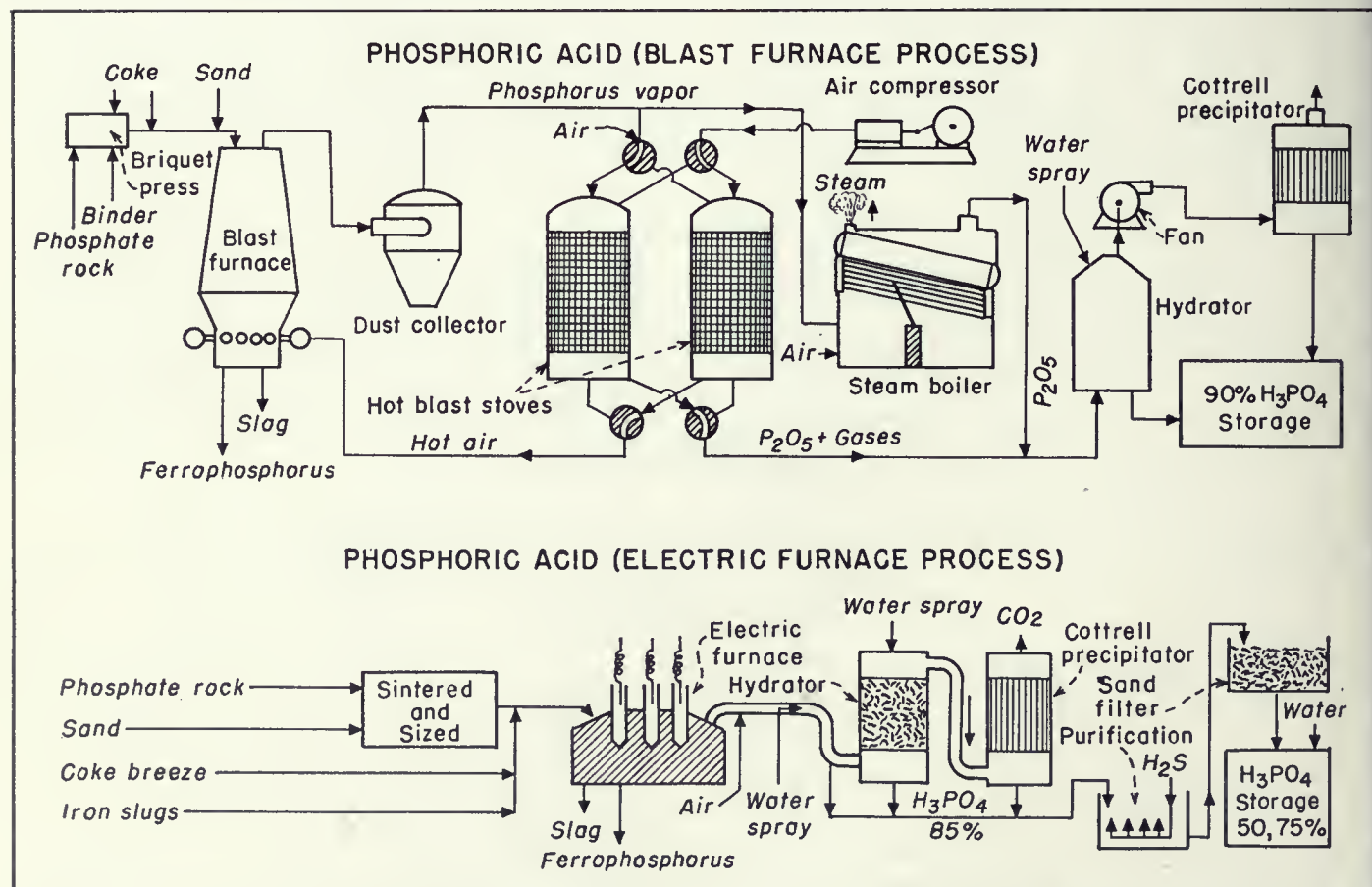


FIGURE 5. Flow sheets showing the production of phosphoric acid by the thermal reduction method. Modified after Olive and Shreve (1947). Published by permission of McGraw-Hill Book Co., Inc.



poration at Permanente. The resulting product was composed of fused western phosphate rock and California serpentine.

Although the prices for phosphate rock are not quoted in trade journals, the phosphate rock mined in Montana, Utah, and Wyoming during 1953 is said to have been valued at an average price of \$7.06 per long ton, rushed, f.o.b. mine (Ruhlman, E. R., 1955, p. 9). This rock averaged about 32 percent  $P_2O_5$  which is equivalent to about 70 percent tri-calcium phosphate. The high-grade phosphate rock produced in Idaho probably was valued comparably. In 1955, the phosphate rock freight rate from Fort Hall, Idaho, to both Los Angeles and San Francisco was \$7.33 per long ton in 40-ton lots. No ready market exists for the known phosphatic rocks of California, as they are of lower grade and in much smaller deposits than those of the western field.

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## PLATINUM AND ALLIED METALS \*

BY WILLIAM B. CLARK

For many years an annual production of a few hundred ounces of platinum and allied metals has been obtained as a by-product of placer gold operations in California. Since 1850, more than 25,000 ounces of these metals have been produced in the state. About three-quarters of this output has been obtained since 1900, when recovery was encouraged by increased prices.

California has consistently led the other states in the production of platinum and allied metals, although Alaska is now the chief domestic source. Domestic sources are limited and have supplied only a small part of the nation's annual requirements. These metals have many strategic uses, and their consumption in non-essential industries was curtailed during World War II.

*Mineralogy and Geologic Occurrences.* Platinum is one of a group of six related precious metals. The others are ruthenium, rhodium, palladium, osmium, and iridium. All have specific gravities in the range of 14 to 22 and high melting points. So-called crude platinum is commonly an alloy of two or more metals of this group. Platinum specimens commonly contain 5 to 15 percent iron and are slightly magnetic. In a finely divided state, platinum is able to absorb large quantities of hydrogen and other gases.

Platinum is white with grayish tinge. When pure, it is very malleable and ductile and takes a very high permanent polish. It occurs as smooth thin flakes, rounded grains, irregular lumps, and occasionally as nuggets. Platinum belongs to the isometric system, and cubic crystals of platinum have been found, but are exceedingly rare. Platinum also occurs in the minerals sperrylite ( $\text{PtAs}_2$ ) and cooperite ( $\text{Pt}(\text{As},\text{S})_2$ ). However, these minerals have not been found in California.

The other members of the group have physical properties similar to those of platinum, although some are harder and more brittle and have higher melting points. Osmium and iridium are most useful as alloying agents with platinum as they give it the hardness necessary for many technical applications. Osmiridium or iridosmine are names applied to the alloy of osmium and iridium which occurs naturally in hexagonal crystals or flattened grains.

Platinum and allied metals are widely distributed throughout the world, but only in a few areas are they recovered commercially. Platinum occurs in extremely small proportions in basic or ultrabasic igneous rocks such as dunite, pyroxenite, serpentine, and norite. The erosion of such magmatic concentrations has provided the placer deposits which have in the past yielded much of the world's production of platinum metal. Placer deposits in the Ural Mountains of Russia have been by far the most productive. The massive nickel-copper sulfide bodies at Sudbury, Canada, the Bushveldt complex, South Africa, and placer deposits of Colombia also are major sources of platinum.

*Localities in California.* The primary source of most of the platinum metal in the placer deposits of California is believed to have been in serpentine and related

basic and ultrabasic igneous rocks. No primary deposits of platinum ore have been found in the state.

The placer deposits that have yielded most of the platinum produced in California are confined largely to two areas: (1) a belt in northwestern California embracing portions of Del Norte, Siskiyou, Humboldt, Trinity, and Shasta Counties; (2) a 180-mile belt paralleling the western Sierran foothills extending from Merced County northwest to Butte County. Production of platinum metals has come largely from connected-bucket dredges (see chapter on gold in this volume) and a few of the larger hydraulic mines.

In nearly all of the placer deposits in the state the proportion of platinum metals to gold is small. This proportion, as indicated by dredge recovery, ranges from  $\frac{1}{3}$  to 1 ounce of platinum metal for every 50 ounces of gold. The placers of the American River, which drains large areas of serpentine and related rocks, have yielded the highest proportion of platinum to gold. Platinum metals recovered along the American River contain 37 to 46 percent platinum and 16 to 35 percent iridium. On the Yuba River, platinum metals contain 60 to 69 percent platinum and 15 to 19 percent osmiridium.

Platinum metals obtained from the Trinity River generally contain more iridium and osmium than platinum. The largest nuggets of platinum metals yet found in California, some of which weighed an ounce or more, were obtained from hydraulic mines near Junction City, Trinity County.

*Mining Methods and Treatment.* Placer platinum is recovered by mechanical means. In California gold-dredging operations, the gold first is removed from the black sand concentrate. The concentrate is then treated by jigging, tabling, and finally hand panning to yield a platinum concentrate. Platinum-group metals which occur in sulfide ores, such as those from Sudbury, Canada, are recovered in the muds from electrolytic cells used in copper, gold, and silver refining. These muds are usually melted to form an impure platinum sponge.

At the refinery, platinum is recovered by chemical means. Dredge concentrates, platinum sponge, sweeps, and scrap metal are dissolved in aqua regia. The solution is filtered, leaving an insoluble residue containing osmium, iridium, and other platinum metals, which are further refined by chemical means. Ammonium chloride is added to the solution and platinum chloride precipitates out. This precipitate is calcined, and the resulting residue, known as "platinum moss," is cleaned and melted into bullion. Much of the refined platinum is marketed in rolled sheets or as wire. Platinum that is used as a catalyst in the chemical or petroleum industry is marketed as a powder or in small pellets.

*History and Production.* In the early days of placer gold mining in California, most of the platinum was discarded because, if salable at all, it brought only a few dollars an ounce. The price of \$4 to \$6 per ounce persisted until 1902, when it began to rise, reaching \$48 per ounce in 1913. The price continued to rise during World War I when the supply from Russia was interrupted,

\* Partly extracted from an article by C. A. Logan in California Div. Mines Bull. 156.



and an all-time high of \$154.23 per fine ounce was realized in 1920. Since World War I, prices have fluctuated greatly but have had little effect on production, as all platinum metals produced are by-products.

Production of platinum metals in California increased during the period 1936-41 because of increased gold dredging. The peak production was reached in 1940 when 1,358 fine ounces were produced in the state. Production decreased greatly during World War II because of curtailment of gold dredging. Also there was less incentive to save the platinum metals because of government control of prices during the war. Immediately after World War II, platinum production increased with an increase in gold dredging. However, since 1948, it has followed the general decline of gold placer operations in California.

**Utilization.** Platinum and allied metals are used for jewelry, in the chemical and electrical industries, in dentistry, and for many other purposes. Nationally in 1955, the chemical industry was the largest user of platinum, iridium, osmium, rhodium, and ruthenium. The electrical industry, however, was the principal user of palladium. In California the electrical industry is the principal consumer of the platinum group minerals, and the chemical industry provides the second largest market. The jewelry industry probably consumes about 10 percent of the platinum group minerals marketed in California.

In the chemical industry, the ability of these metals to absorb large quantities of gases renders them as valuable catalysts. Catalytic uses include the manufacture of nitric and sulfuric acids, hydroxylation, and in the production of high-octane gasoline from low-grade or natural gasoline. Because of their great resistance to corrosion, oxidation, and acids, the metals are widely used in laboratory equipment and as insoluble anodes in electroplating.

In the electrical industry, alloys of the platinum metals are used in the manufacture of spark plug electrodes, resistors, fuses, and contacts for relays, magnetos, and voltage regulators. In dentistry, platinum or palladium is alloyed with gold to form a dental metal that resists tarnish, is strong, and responds to age-hardening treatment.

In jewelry, various alloys of the platinum metals are used in the manufacture of rings, pins, and watches. Platinum also is a constituent of salts used in photography, and is used as a coloring matter in ceramics.

**Markets.** Although relatively small amounts of platinum metals are produced in California, large quantities of the refined metals are consumed in the state. Crude platinum, both domestic and foreign, is usually sold in lots directly to the refiners. California dredging com-

panies usually sell one or two year's production in one lot to the highest bidder. The principal platinum refiners in the United States are in New Jersey and Pennsylvania. There are refiners in San Francisco and Los Angeles. At present, Canada is the principal source of imported platinum. Substantial amounts also are imported from the Netherlands and the United Kingdom. A considerable amount of the metals is recovered from scrap and sweeps. The refined metal thus obtained is sold by refiners directly to jewelry manufacturers, the electrical and chemical industries, and dental supply houses. The total amount of platinum consumed annually in California is difficult to determine as statistical control cannot easily be established in the marketing chain, but this consumption probably is measurable in tens of thousands of ounces. In December, 1955, the quoted prices of the metals were as follows: platinum, per ounce troy, \$104.00; iridium, per ounce troy, \$110.00; rhodium, per ounce troy, \$125.00; palladium, per ounce troy, \$24.00; ruthenium, per ounce troy, \$55.00; and osmium, per ounce troy, \$100.00.

In 1955 clean scrap platinum was being sold to refiners in California for \$70 per ounce and newly refined platinum was being marketed in the range of \$83.00 to \$87.00. The difference in price between the scrap and newly refined material included the cost of refining and sales profit. In general, the refineries will consider the purchase of platinum-bearing ores or concentrates in which the platinum content per pound of material is valued at one dollar or more.

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## PUMICE, PUMICITE, PERLITE, AND VOLCANIC CINDERS

By CHARLES W. CHESTERMAN

The commercial production of pumice and pumicite in California began in 1909, and by 1955 had risen to an annual total of 88,825 short tons valued at \$416,309, the second highest output among the states. Expanded perlite was first produced in California in 1945, and has been obtained in large tonnages since the late 1940's. The mining of volcanic cinders in California started about 1916, and by 1955 the annual production of volcanic cinders had risen to 708,481 short tons valued at \$683,151. Pumice, volcanic cinders and expanded perlite have many uses, especially as lightweight aggregates. Expanded perlite also is employed in the chemical and other industries. Pumicite is used principally as a carrier in pesticides and insecticides for agricultural sprays. The tremendous growth of population and industry in California since the close of World War II has brought a marked increase in the use of these materials.

### GENERAL GEOLOGY

Pumice, pumicite, and perlite are volcanic glasses formed during the rapid chilling of granitic to intermediate magmas. They commonly occur together and exist in California in regions of Tertiary and Recent volcanism which cover extensive parts of the state. The pumice, pumicite, and perlite deposits that exist today are relatively recent in age because, with advancing time, the glassy rocks devitrify and most surficial deposits are eroded away. The distinction between pumice and pumicite is one of particle size rather than structure and composition.

Pumice is a pumiceous glass that occurs in fragments ranging in size from about  $\frac{1}{8}$ -inch to large masses as much as 10 feet across. The cells in pumice are spherical, tubular, or irregular in shape. They range in maximum dimension from a very small fraction of an inch to as much as several inches. Most pumice is pale gray to white in color. Crystals of quartz, feldspar, biotite and hornblende locally are present as phenocrysts.

Pumicite, also known as volcanic ash, consists of finely divided glass particles less than  $\frac{1}{8}$ -inch in diameter. These are blown from volcanoes, and during air transport the particles are crudely to moderately well classified to form deposits containing fragments of rather uniform size. Pumicite ranges in color from white to red.

Pumice rarely forms separate rock masses, but generally occurs in fragments admixed with mineral grains and other rock fragments in varying proportions. Masses of pure pumice, however, are found as tops of flows and domes of obsidian. Material that consists largely of angular pumice fragments, ranging up to 6 inches in diameter and in a matrix of pumicite, is called tuff-breccia. Pumice breccia, on the other hand, contains only a minor proportion of the finer-grained pumicite matrix. Pumice lapilli-tuffs, consist mostly of pumice fragments in the size range of  $\frac{1}{8}$ -inch to  $\frac{1}{4}$ -inch.

Most of the aggregate pumice mined in California is obtained from tuffs, tuff-breccias, and pumice breccias, and on the basis of their mode of deposition and origin, they are classified as follows: (1) subaerial deposits—those deposited on dry land—characterized by lack of bedding and sorting; (2) subaqueous deposits—those

deposited in standing water—characterized by bedding and interbeds of silt, sand, and gravel; (3) Nuée Ardentes deposits characterized by lack of bedding and a very wide range in grain size from impalpable dust to block several yards across; and (4) reworked deposits characterized by graded bedding, crossbedding, and rounded fragments.

Perlite, strictly defined, is a glassy volcanic rock characterized by an "onion skin" fracture, and which breaks into minute spherical fragments. Perlite, as well as many other siliceous volcanic glasses, will, upon rapid controlled heating, expand into a frothy, white material that resembles pumice and is valued as a lightweight aggregate. In an industrial sense, all expansible volcanic glass is referred to as perlite. In general, the chemical composition of perlite ranges from rhyolitic to dacitic; most perlites contain from 3 to 5 percent water. Most perlite is pale gray, but some is black, reddish-brown, or even green. Phenocrysts of quartz, feldspar, biotite, and hornblende commonly are present, and in some deposits are abundant enough to render the perlite unsuited to commercial use.

Many perlite deposits are flows associated with thick accumulations of tuffs and flows of other volcanic rocks. In most places, flows of perlite-bearing volcanic rocks are so recent that they are nearly horizontal, but locally they are moderately deformed. Individual flows of perlite range in thickness from a few feet to several tens of feet, and commonly cover several square miles. Bodies of perlite also occur as domes, dikes, and as selvages bordering andesitic and rhyolitic intrusive bodies.

Most perlites are formed from obsidian, or other glassy volcanic rock, by a process which the writer has referred to as "perlitization". By this process a volcanic glass, originally containing only a few hundredths percent water, becomes fractured and brecciated, and hydrated to perlite. The completeness of the hydration of the glass depends largely upon the degree of access permitted the water vapor (Wright, Chesterman and Norman, 1954, p. 67). The water necessary for perlitization appears to have been derived partly from the intruded rocks and partly from rhyolite bodies that were being emplaced nearby.

Volcanic cinders are vesicular masses of lava which resemble clinker produced in a furnace. They consist of small crystals of plagioclase and pyroxene enclosed in a mesh of still smaller crystals of these minerals and of subordinate dark-colored volcanic glass. In California volcanic cinders are mined from cinder cones which formed around central openings or along fissures during periods of explosive volcanic activity. Most cinder cones are nearly circular in plan, range from a few hundred feet to several thousand feet in diameter, and some are as much as 500 feet high. The cinder deposits are stratified and consist mostly of fragments that range from a fraction of an inch to several inches in diameter. Volcanic bombs are common in most cinder deposits, and dikes of basalt or andesite have been found in some cones. The cinders are generally red, brown, dark-gray, or black in color.



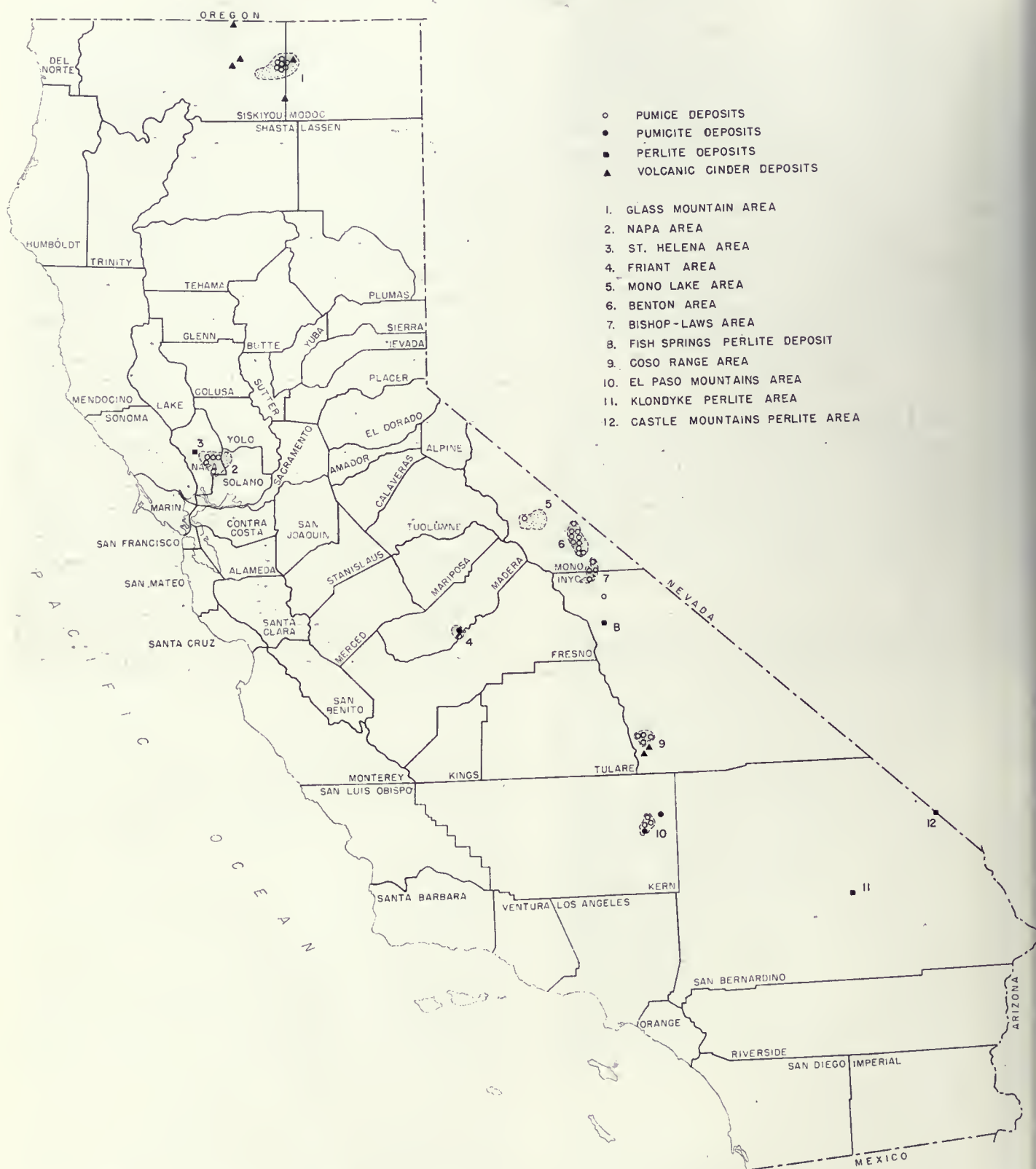


FIGURE 1. Map of California showing location of principal mines and producing areas for pumice, pumicite, perlite, and volcanic cinders.





FIGURE 2. Fench pumice pit, Glass Mountain area, eastern Siskiyou County. Pumice is mined from a mantle-like layer of loosely consolidated pumice tuff-breccia (P) which covers all older volcanic rocks, but which is itself overlain locally by a flow of obsidian (O). Observer faces southwest.

#### DEPOSITS OF PUMICE, PUMICITE, AND VOLCANIC CINDERS IN CALIFORNIA

Although deposits of pumice, pumicite, and volcanic cinders are numerous and widespread in California, the commercial production of these materials has been obtained mostly from the following areas: (1) Glass Mountain area, eastern Siskiyou County; (2) Coso Range area, western Inyo County; (3) Bishop-Laws area, eastern Mono and northern Inyo Counties; (4) Benton area, eastern Mono County; (5) Napa area, northeastern Napa County; (6) Mono Craters area, western Mono County; and (7) the Friant area, southern Madera County. Substantial amounts of these materials also have been produced from properties in other widely scattered areas.

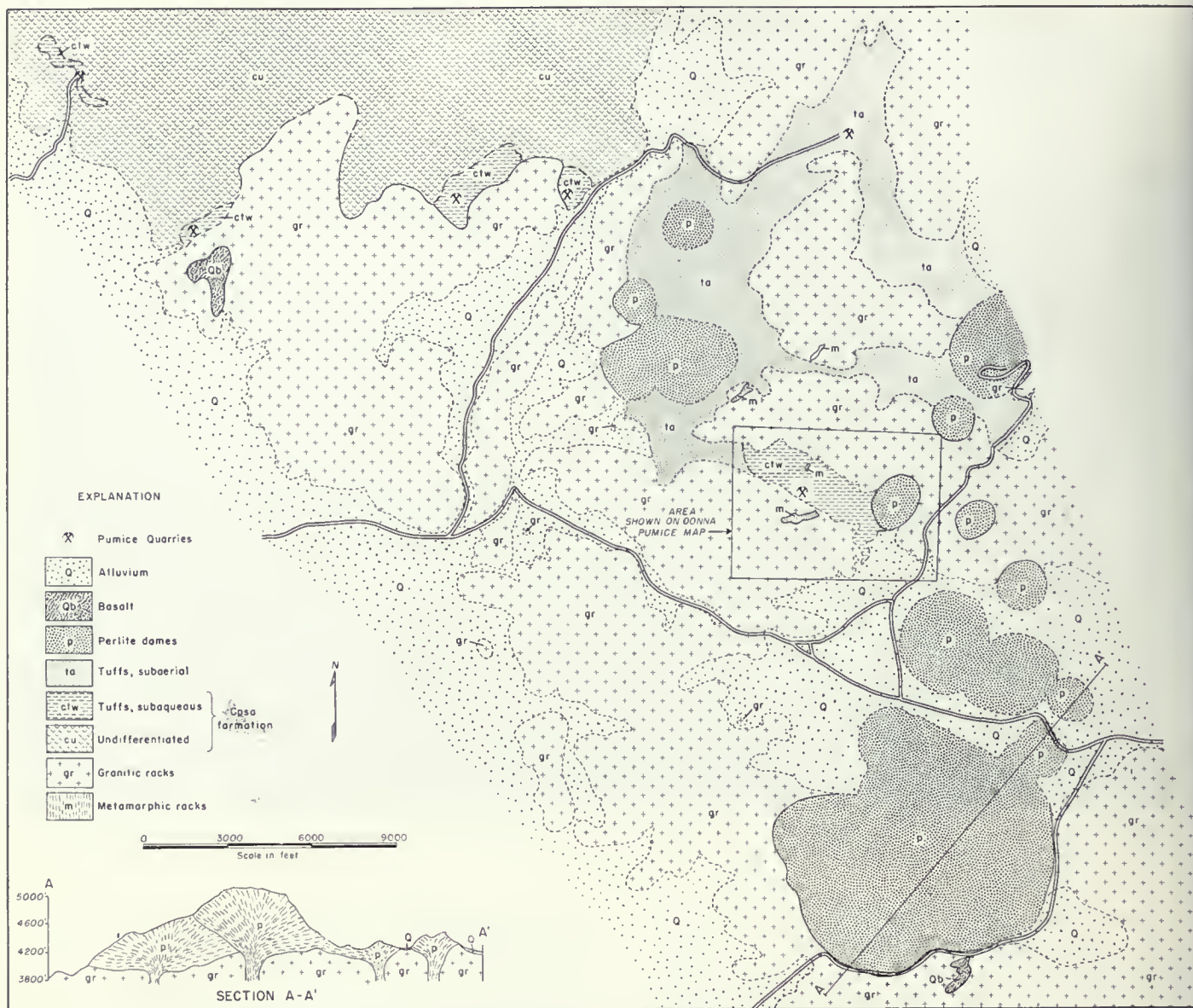
The pumice deposits within a given area ordinarily have similar characteristics. The Benton area, however, contains deposits of land-laid, water-laid and reworked pumice.

**Glass Mountain Area.** The Glass Mountain area of eastern Siskiyou County contains lava-covered mountain peaks and plateaus, volcanic cinder cones, and small alluviated valleys and basins. The pumice deposits in this area were first systematically explored in 1935, and

the first pumice was shipped in 1936. Large-scale production began in 1947, and in 1951 the total annual production had risen to about 35,000 tons of pumice, which was used mainly for aggregate purposes.

Glass Mountain, a prominent peak near the eastern part of Siskiyou County, consists largely of volcanic glass emplaced within the last 1200 years (Chesterman, 1955, pp. 418-424). The mountain is composed of two flows. The lower and earlier flow is a composite flow of rhyolite-dacite, whereas the upper and later flow is rhyolite obsidian. The obsidian flow has a vesiculated upper surface and is mined for scouring brick pumice. Spreading to the northeast from Glass Mountain is a fan-shaped mantle of loosely consolidated pumice tuff-breccia which is at least 60 feet thick at Glass Mountain, but which thins to a few inches at Tionesta, a small siding on the Great Northern Railroad, about 10 miles to the east of the mountain. At Glass Mountain, where most of the pumice has been mined, the tuff-breccia is in two layers which indicate at least two separate periods of pumice deposition. The upper layer, which is the thicker and more productive, is well exposed in numerous quarries and test pits, and ranges from a few feet to at least 30 feet in thickness. The lower tuff-breccia layer is thinner, and rests directly upon flows of older basalt.





GEOLOGIC MAP OF THE COSO RANGE PUMICE AND PERLITE AREA, INYO COUNTY, CALIFORNIA

FIGURE 3.

The pumice in both layers is grayish-white in color, and occurs in angular fragments that range in size from dust-like particles to lumps and bombs 6 inches in diameter. The tuff-breccia contains minor pink rhyolite, dark-brown basalt, and black obsidian, but these do not appear to be deleterious in use of the pumice as aggregate in concrete products.

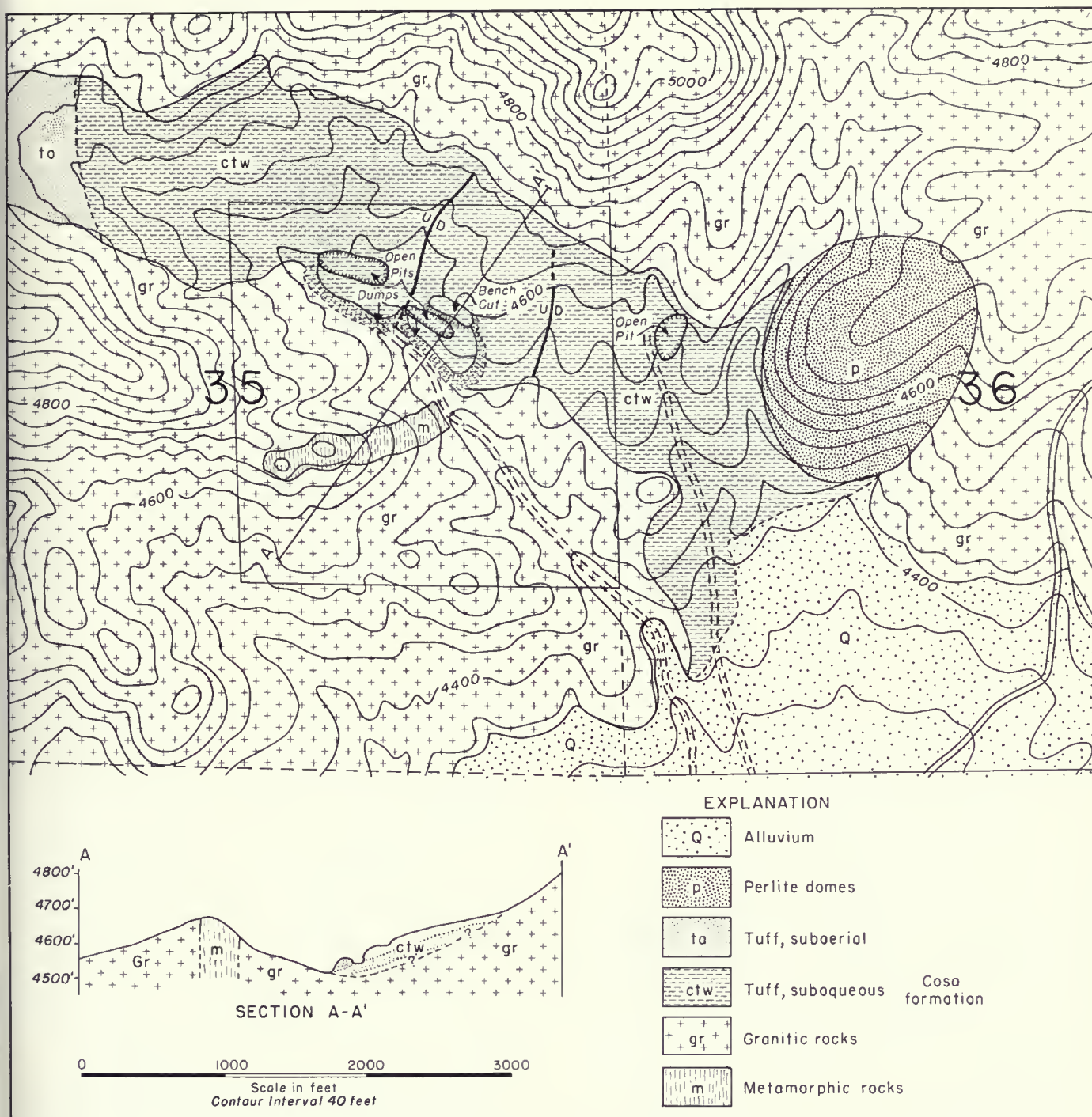
The pumice, which has virtually no overburden, is mined by open pit methods by use of bulldozers or tractor elevators. It is trucked to Tionesta where it is processed for use as aggregate and loaded into gondola cars for shipments to markets in central and northern California and southern Oregon.

Pumice has been actively mined from about eight quarries in the Glass Mountain area. Of these, the largest

is the Fouch quarry of the Thompson Pumice Company which in 1955 measured about 700 feet long, 300 feet wide, and about 12 feet deep.

Pumice suitable for the manufacture of scouring bricks has been produced from the top of Glass Mountain since 1936. This pumice occurs as a crust on the surface of the obsidian flows and forms jumbled masses of angular blocks associated with black obsidian and coarsely vesiculated obsidian. The scouring brick pumice has been mined to a depth of at least 10 feet, and the pumiceous material extends to an undetermined depth below this. Choice blocks are gray in color, commonly range in maximum dimension from one foot to three feet and are relatively free from obsidian. The pumice mined by U. S. Pumice Supply Company is loaded into trucks by use of tractor elevator and hauled to a processing plant near





GEOLOGIC MAP OF THE DONNA PUMICE DEPOSIT,  
COSO RANGE PUMICE AND PERLITE AREA, INYO COUNTY, CALIFORNIA

FIGURE 4.

Tulelake where it is cut into "Grillmaster" scouring bricks.

At Little Glass Mountain, about 10 miles west of Glass Mountain, an extensive deposit of pumice occurs in a loosely consolidated pumice tuff-breccia layer which ranges from a few feet to 10 feet in thickness. The tuff-breccia has no overburden and consists primarily of light-gray angular pumice fragments that range in size

from  $\frac{1}{16}$ -inch to 3 inches. Although pumice was mined in this area as early as 1905, the output has been small in comparison with that obtained in the Glass Mountain area. The latest recorded production was in 1935 (Ave-  
rill, 1935, p. 335), but a small tonnage has been produced for research purposes since then.

Volcanic cinders have been extensively quarried at East Sand Butte, a typical stratified cinder cone about



4 miles north of Tionesta, Modoc County. The cone rises about 300 feet above a comparatively level plain of basalt flows. The cinders are angular, black to red in color, and range from  $\frac{1}{4}$ -inch to 3 inches in diameter. They are mined in open pits with bulldozers and are used primarily as ballast and bankwidening for the Great Northern railroad in California and Oregon.

Volcanic cinders also are being quarried for railroad ballast by the Southern Pacific Railroad from cinder cones in the northern part of Siskiyou County, north of Mount Shasta. The principal operation is at Kegg where a cinder cone, which formerly was about 75 feet high and at least 1,000 feet in diameter, has been almost completely leveled. The cinders are stratified, basaltic in composition, red to black in color, and range from  $\frac{1}{4}$ -inch to several inches in diameter. The central portion of throat of the cone is filled by an irregular plug-like mass of basalt.

Volcanic cinders are being quarried from another cinder cone near Hotlum, Siskiyou County, also north of Mount Shasta. These cinders are basaltic in composition, dark gray to black in color, well stratified, angular, and range in size from  $\frac{1}{4}$ -inch to 4 inches. They are marketed, at Yreka and the northern part of the Sacramento Valley, for use as aggregate in building blocks.

*Coso Range Area.* The Coso Range, in southwestern Inyo County, contains a central core of granitic and metamorphic rocks which is overlain in upward sequence by (1) alluvial gravels, (2) tuffs and lacustrine sediments, and (3) flows of andesite and basalt. This sequence comprises the Coso formation (Schultz, 1937, p. 79) of late Pliocene or early Pleistocene age. Pumiceous tuffs are well exposed on the southern, western, and northern flanks of the Coso Range, but most of the pumice mined in this area has been obtained from tuffs exposed on the western and southern flanks of the range. The Coso Range also contains extensive deposits of volcanic cinders and perlite.

Pumice was first mined in the Coso Range area in 1920, but these early shipments were small and were marketed in southern California principally for use as an abrasive. The large-scale production of pumice, however, began in 1946, and by 1955 well over 400,000 cubic yards of pumice valued at more than \$1,000,000 had been mined from several pumice properties. This pumice was used mostly as aggregate for concrete which finds wide acceptance throughout the country. Volcanic cinders were first mined in the Coso Range area prior to 1948, and by 1955 the deposits had yielded a total of about 250,000 tons obtained mostly from two operations.

The tuffs in the Coso Range are of both subaqueous and subaerial origin, but most of the pumice mined in this area has been obtained from subaerial deposits. Although each tuff has distinctive features, the pumice in all of them is similar in many respects and has been used principally for aggregate in pre-cast and monolithic concretes.

Most of the tuffs of subaqueous deposition are well stratified and commonly contain pumice beds inter-layered with gray, moderately well consolidated, pumiceous sandstone. The tuff beds range in thickness from one foot to 15 feet, and in several places they have an aggregate thickness of 100 feet. The tuffs are made up

of pumice fragments that are white, angular to rounded, and range from  $\frac{1}{4}$ -inch to 2 $\frac{1}{2}$  inches in diameter. The pumice contains phenocrysts of deep-brown biotite, black hornblende, and white feldspar. Scattered irregularly throughout the tuffs are rounded and angular boulders of granite, hornblende andesite, and dark mica schist.

The tuffs of subaerial deposition are surficial deposits covered largely by pumiceous and sandy soils as much as 20 feet in thickness. The tuffs show a poorly defined bedding and an almost total lack of sorting. The pumice layers range in thickness from 1 foot to 10 feet, and are composed of white, angular fragments that range from  $\frac{1}{4}$ -inch to 2 $\frac{1}{2}$  inches in diameter. The pumice contains phenocrysts of dark-brown biotite, black hornblende, and glassy feldspar. Boulders of hornblende andesite, dark mica schist and weathered granite are scattered throughout the tuff.

Although as many as four firms have quarried pumice in the Coso Range area, only two operations were active in 1955. The largest operator, the Crownite Corporation, has quarried pumice from both subaerial and subaqueous tuffs, although the present output is obtained from a deposit of subaerial deposition. The size of this deposit is not known, but pumice has been mined to a depth of 30 feet. The other operator, Henry Babineau, quarried pumice from a layer of subaqueous tuff poorly exposed along the west flank of the Coso Range. The actual thickness of the tuff layer is not known, but thicknesses up to 30 feet have been exposed in quarry faces and test pits.

In 1955, volcanic cinders were being quarried from two cinder cones at the southern end of Rose Valley, about 4 miles north of Little Lake, Inyo County. Two cinder producers, Redlite Aggregates Incorporated and Volcanic Cinder Company operate quarries on the south side of Red Cinder Mountain, and the third, Paul Splane, operates a quarry on the north side of another cinder cone about 2 miles to the northeast. The cinders at both localities are basaltic in composition and contain small lath-shaped crystals of labradorite set in a finer-grained groundmass of pyroxene, labradorite, and dark-brown volcanic glass. The cinders are loosely consolidated, dark reddish-brown in color, and range in size from  $\frac{1}{8}$ -inch to about 6 inches in diameter. Volcanic bombs and large lump-like masses of agglutinated cinders as much as several feet in diameter are common in the cones. The total reserves of mineable cinders probably exceed several tens of millions of cubic yards.

*Benton Area.* Most of the early production of pumice in California was obtained from extensive pumice deposits near Benton, eastern Mono County. The pumice in this area occurs in tuff layers composed of detrital pumice fragments discharged from volcanic centers that probably lay to the west. Although both subaqueous and subaerial tuffs exist in the area, most of the current output is of the subaerial type. In the late 1940's, however, large tonnages of pumice were mined from deposits that contain, in addition to subaqueous pumice, layers of reworked pumice.

The tuff layers rarely dip more than 7 degrees, and range in thickness from one foot or less to several tens of feet. Fortunately, much of the pumice lies near the surface and is overlain only by sandy and pumiceous





FIGURE 5. View of the Splane volcanic cinder operation near Red Cinder Mountain, Inyo County. The red volcanic cinders are obtained from a cinder cone (C), treated at plant (P), and stored in storage yard (Y). Observer faces south.

soil which ranges from a few inches to 10 feet in thickness.

The pumice fragments in all of the tuffs are grayish-white and range from  $\frac{1}{16}$ -inch to 4 inches in diameter. Most of the fragments are angular, but in the subaqueous deposits some are rounded. Sand composed principally of angular grains of quartz and feldspar, constitute as much as 5 percent of the tuffs. Although scattered throughout the tuffs, the sand commonly is concentrated in a narrow zone at or near the base of the tuff layers. Angular to rounded boulders of granite and dark mica schist also occur in the tuffs. These and the sand are, however, removed from the pumice by simple screening operations.

Although the deposits of pumice in the Benton area had been known for many years, they were first worked in 1926. By 1948, eight firms were mining aggregate pumice in the Benton area at a combined rate of several tens of thousands of tons each year. The pumice has been mined by both open pit and underground methods. Underground mining ceased about 1945. All of the output in 1955 was recovered by a single firm—Cowan and McGraw—from open pits. The pumice was being obtained from a layer of subaerial tuff that averages about 12 feet thick and which has been widely prospected by numerous test pits and cuts. Bulldozers are used to mine and push the pumice to screening plants at or near the pits.

**Bishop-Laws Area.** The Bishop-Laws pumice area, in Mono and Inyo Counties, includes a part of Owens Valley and extends northward along the west slope of the White Mountains from Big Pine to Sacramento Canyon. The area also embraces the southeastern part of

the Volcanic Tableland, a dissected mesa a few miles north of Bishop.

Pumice mining in the Bishop-Laws started about 1926 with the opening of quarries along the southeastern margin of the Volcanic Tableland. Since then pumice has been mined at 8 localities throughout the area, but in 1955 only two were active. One of these is operated by the Bishop Hardware Company which mines pumice along the southern margin of the Volcanic Tableland and markets it as concrete aggregate. The other is operated by Insulating Aggregates and has been in almost continuous operation since 1926. This concern produces aggregate for acoustical plaster and stucco from a tuff layer along the eastern margin of the Volcanic Tableland. The early output was used in making cleansing compounds and scouring soaps, and for aggregate in stucco and acoustical plaster (Tueker, 1927, p. 403). During World War II, abrasive pumice was produced from one deposit on the west flank of the White Mountains.

In the Bishop-Laws area, the pumice is obtained from subaqueous and subaerial deposits, and some of nuée ardente origin; most of the output, however, has been mined from deposits of subaqueous deposition. The reserves of pumice in this area are measureable in millions of cubic yards.

Pumice deposits of the nuée ardente type are well exposed along the southeastern and southern margins of the Volcanic Tableland, about 5 miles north of Bishop. The deposits are confined mostly to a layer of loosely consolidated tuff, a part of the Bishop tuff (Quaternary), about 30 feet thick that is commonly overlain by a denser phase of the Bishop tuff. The tuff layer is loosely



consolidated and contains more pumicite than pumice. The fragments within the layer range in size from dust-like particles to well-rounded lumps as much as 4 inches in diameter. The pumice is pale, pinkish-brown and contains scattered phenocrysts of quartz and sanidine. That portion which passes through a  $\frac{5}{8}$ -inch screen is saved, the remainder is waste.

Pumice of subaqueous deposition is widespread along the eastern margin of the Volcanic Tableland where it occurs in a nearly horizontal layer about 15 feet thick. It lies upon crossbedded deltaic sands and gravels and is overlain by loosely consolidated Bishop tuff. The pumice fragments are angular, white in color, and range in size from  $\frac{1}{8}$ -inch to 2 inches in diameter.

Subaqueous pumiceous tuff layers also are exposed along the west slope of the White Mountains and are interbedded with layers of fanglomerate as much as 20 feet thick. The tuff layers range in thickness from a few feet to 30 feet, show maximum exposed lengths of several hundred feet, and consist of several beds of pumice interbedded with thin layers of pumicite and silica sand. The pumice fragments are angular, white in color, and range from  $\frac{1}{8}$ -inch to 3 inches in diameter. Bedding is prominent in the tuffs, and the dip is toward the west and southwest from 2 to 10 degrees.

The pumice in the Bishop-Laws area is mined by open pit methods. The overburden is stripped away by bulldozers which also mine and push the pumice to the screening plants, commonly situated near the pits.

**Mono Craters Area.** In the west-central part of Mono County, pumice for scouring bricks is being quarried from two of the several domes in the chain of late Quaternary volcanic domes known as the Mono Craters. These volcanic domes consist mostly of obsidian and rise abruptly from a plain covered by a mantle of loose pumiceous ejecta. The domes are steep sided and their tops are covered by a chaos of jumbled blocks of pumice and pumiceous obsidian that range from one foot to four feet across. The openings in the pumice are tubular and commonly drawn-out parallel to a flow banding. The pumice is brownish-gray on the weathered surface, but on a fresh surface, it ranges from dark to light gray. From this rock the scouring bricks are fashioned.

All mining is by open pit methods. Blasting is required to break down some of the pumice from the quarry walls. Selected material is loaded into trucks by tractor loaders and hauled about 8 miles to a sawing plant at LeeVining where it is trimmed and cut into scouring bricks of several sizes.

The pumice which mantles the ground around the Mono Craters remains unmined, principally because of its remoteness. The maximum thickness of this mantle is not known, but it has been exposed to depths exceeding 10 feet at several widely spaced test pits and in a few deep road cuts, and appears to contain very large reserves of aggregate-grade pumice. This pumice is white, and occurs in angular fragments that range from  $\frac{1}{8}$ -inch to 3 inches in diameter. The U. S. Pumice and Supply Company is the only firm mining and processing pumice in the Mono Craters area.

**Napa Area.** An area along Sarca Creek about 4 miles northeasterly from Napa, Napa County, first yielded

commercial quantities of pumice in 1932, and by 1952 the annual output had increased to several tens of thousands of short tons. The pumice is used primarily as aggregate in lightweight concrete.

In the Napa area the pumice is mined from layers of massive lapilli tuff and tuff-breccia of late Pliocene age. These layers of pyroclastic rock are as much as 150 feet thick and generally dip gently southwestward. They consist mostly of angular, grayish-white pumice fragments, but also contain minor lapilli of black obsidian, basalt bombs as much as 3 feet across, angular fragments of red scoria, and clay formed mostly by the alteration of fine-grained tuff.

All mining is by open pit methods. Bulldozers scrape away a thin overburden of soil and push the pumice to processing plants commonly at or near the pit. Pumice has been mined at seven localities throughout the area, but in 1955 only one operator, C. Cicero, was active. Pumice for aggregate purposes is obtained from a layer of massive tuff-breccia which is as much as 50 feet thick.

**Friant Area.** In the Friant area, in southern Madera County, pumice and pumicite have been produced from tuff layers in the Friant (Pleistocene?) formation, which crops out in low, flat-topped hills north and east of the town of Friant on the San Joaquin River. Pumicite was first mined in this area in or about the year 1904 and was utilized as a polishing agent. This operation lasted only a few years. In 1914, attempts again were made to mine the pumicite and, at a small plant in Fresno, it was made into polishing powder and scouring soap. In 1927, however, development work was started on several pumicite deposits and much of the pumicite mined was utilized as an admixture with cement in concrete. Several of the properties south of the San Joaquin River subsequently were covered by waters of the Friant Dam, and are therefore not accessible to mining.

The mining of pumice in the Friant area started about 1930. The pumice was and is still being used as aggregate in concrete building blocks, shingles, and roofing tile. Most of the present output of pumicite from the Friant area is consumed in agricultural uses, especially as a diluent and carrier for pesticides and insecticides.

The Friant formation is flat-lying and consists mostly of a sequence of lacustrine and fluvial deposits of silt, sand, pumiceous sand, gravel, and thinly bedded pumicite tuffs and lapilli tuffs (Trauger, 1950, p. 1531) which rests upon granite. At the bottom are layers of pumicite interbedded with thin layers of silt, clayey sands, and sands. These are overlain by a layer of sandstone which grades upward into pumiceous sandstone that locally contains lens-like layers of pumice lapilli-tuff. The pumicite layers range in thickness from a few inches to 6 feet; locally they have a combined thickness of about 150 feet. The pumicite is colored grayish-white to brick-red, and consists mostly of flat, angular glass particles that range from 0.001 to 0.015 mm. in diameter. The pumice fragments in the pumiceous sandstone and pumice lapilli-tuff are sub-rounded, white to pale pinkish-brown, and range from  $\frac{1}{8}$ -inch to 4 inches in diameter. The pumiceous sandstone and pumice lapilli-tuff layers have an aggregate thickness of about 30 feet, and ordinarily have a thin soil covering.



Both the pumicite and pumice are mined by open pit methods, although pumicite formerly was obtained by underground methods. Minor blasting is required to break down the more firmly compacted pumicite. The pumicite is loaded into trucks with a small shovel or bulldozer and hauled to processing plants situated at the deposits. The pumice is mined by bulldozer which also pushes the pumice to screening plants at the pits.

The pumice and pumicite have been mined at seven localities throughout the Friant area, but in 1955 only three were active. Two firms—California Industrial Minerals Company and Ol' Rebel Minerals, Incorporated—mine and process pumicite. Pumicite is obtained from extensive deposits whose reserves, at each operation, are in excess of several hundreds of thousands of tons. Pumice is being mined only by the Pumice and Pumicite Mining Company which operates an extensive deposit of pumiceous sandstone that averages about 30 feet thick and which contains reserves of at least several hundreds of thousands of tons.

*Miscellaneous Deposits of Pumice, Pumicite, and Volcanic Cinders.* Pumice has been produced from other tuff layers scattered throughout California. The Williams Brothers mine, about 18 miles northwest of Bartow, San Bernardino County, has yielded pumice for aggregate purposes from a thick and extensive layer of consolidated tuff. Pumice for aggregate purposes also is being produced from pumice conglomerates at Obsidian Butte, about 10 miles northwesterly from Calipatria, Imperial County. Volcanic ash deposits at Shoshone, Inyo County and in Last Chance Canyon, Kern County, were for many years important sources of pumicite but were idle in 1955. Tuffs in the Last Chance Canyon area of eastern Kern County are mined for acoustical plaster aggregate and abrasive pumice.

#### MINING METHODS

In 1955, as already indicated, all of the active pumice, pumicite, and volcanic cinder operations in California were open pits. The maximum possible size of the pit is determined largely by the size of the deposit and the amount of overburden which must be removed. The overburden, which commonly ranges in thickness from a few inches to several tens of feet is stripped away with bulldozers or carryalls. From deposit to deposit, the overburden differs in composition from loosely consolidated pumiceous soil to firmly compacted and cemented tuff. In general the thickness of overburden is less important than the thickness of mineable pumice to be exposed. The removal of 10 feet of overburden from a 50 foot layer of pumice, for example, ultimately may prove no more costly per ton of pumice mined than the removal of one foot of overburden from 5 feet of pumice. Once the pumice, pumicite, or volcanic cinder deposits are exposed, they are mined with a bulldozer, power shovel, dragline, or tractor loader. At some of the operations the processing plant is at or near the pit, at others the plants are on rail facilities as much as 10 miles from the pit. Most of the pumice, pumicite, and volcanic cinder deposits require no blasting. Where blasting is required, care is taken only to break the material from the walls of the open pits and not into fragments too small to be usable.

#### PROCESSING OF PUMICE, PUMICITE, AND VOLCANIC CINDERS

Processing facilities range from a single screen, over which is fed crude, quarry-run material, to plants that contain primary and secondary crushers and numerous screens and that yield commercial materials within narrow size specifications. The preparation of pumice and volcanic cinders for use as concrete aggregate commonly consists of running the material over a screen with  $\frac{3}{4}$ -inch openings. The treatment of pumice for acoustical granules, plaster aggregate, and abrasive uses consists, in addition to primary crushing and screening, of secondary crushing in a hammer mill, drying, and screening. The processing of pumicite includes drying and multiclone collecting. In the course of drying pumicite, the bond which holds the particles together is broken. A multiclone dust collector recovers most of the pumicite which averages about 85 percent minus 325 mesh. The still finer material is collected in baghouses.

Table 1. Typical products of pumice, pumicite, and volcanic cinders; their sizes and methods of processing.

Product	Size in inches or mesh	Method of processing
Insulating aggregate for pre-cast or monolithic concretes	$-\frac{3}{4}, +\frac{5}{16}$	Crushing in jaw crusher and screening
Pea gravel for block aggregate	$-\frac{5}{16}$ , to pan	Crushing in jaw crusher and screening
Gunnite aggregate-----	$\frac{3}{16}$ , to pan	Crushing in jaw crusher and screening
Plaster aggregate-----	$-\frac{1}{8}, +\frac{1}{16}$	Secondary crushing in hammer mill, drying, and screening
Stucco aggregate-----	$-\frac{1}{8}$ , to pan	Secondary crushing in hammer mill, drying and screening
Floor sweeping compound	-9, +50 mesh	Secondary crushing in hammer mill, drying, and screening
Paint filler-----	-20, +50 mesh	Secondary crushing in hammer mill, drying, and screening in a special type of mill
Abrasive for cleaners-----	-20, +50 mesh	Secondary crushing in hammer mill, drying, and screening in a special type of mill
Abrasive for dental trade	-80, +200 mesh	Secondary crushing in hammer mill, drying, and screening in a special type of mill
Pozzolan-----	-200, +325 mesh	Secondary crushing in hammer mill, drying, and screening in a special type of mill

#### DEPOSITS OF PERLITE IN CALIFORNIA

Although there are many deposits of perlite in California, most of the output of crude perlite in the state has been obtained from deposits in four areas: (1) Fish Springs area, Inyo County; (2) Klondyke and (3) Castle Mountain areas, San Bernardino County; and (4) St. Helena area, Napa County. In 1954, these areas yielded a total of about 16,000 tons of crude perlite.

*Fish Springs Area.* The Fish Springs perlite area is in western Inyo County, about 7 miles south of Big Pine. Here a single perlite deposit forms a Recent volcanic dome which rises as a conspicuous hill about 200 feet high and is surrounded by outwash granitic debris derived from the east face of the nearby Sierra Nevada. The dome is elongated in an east-west direction and is capped by pumiceous perlite that grades downward into less pumiceous perlite. The zone of mineable perlite is about 80 feet thick, and is underlain successively by brecciated



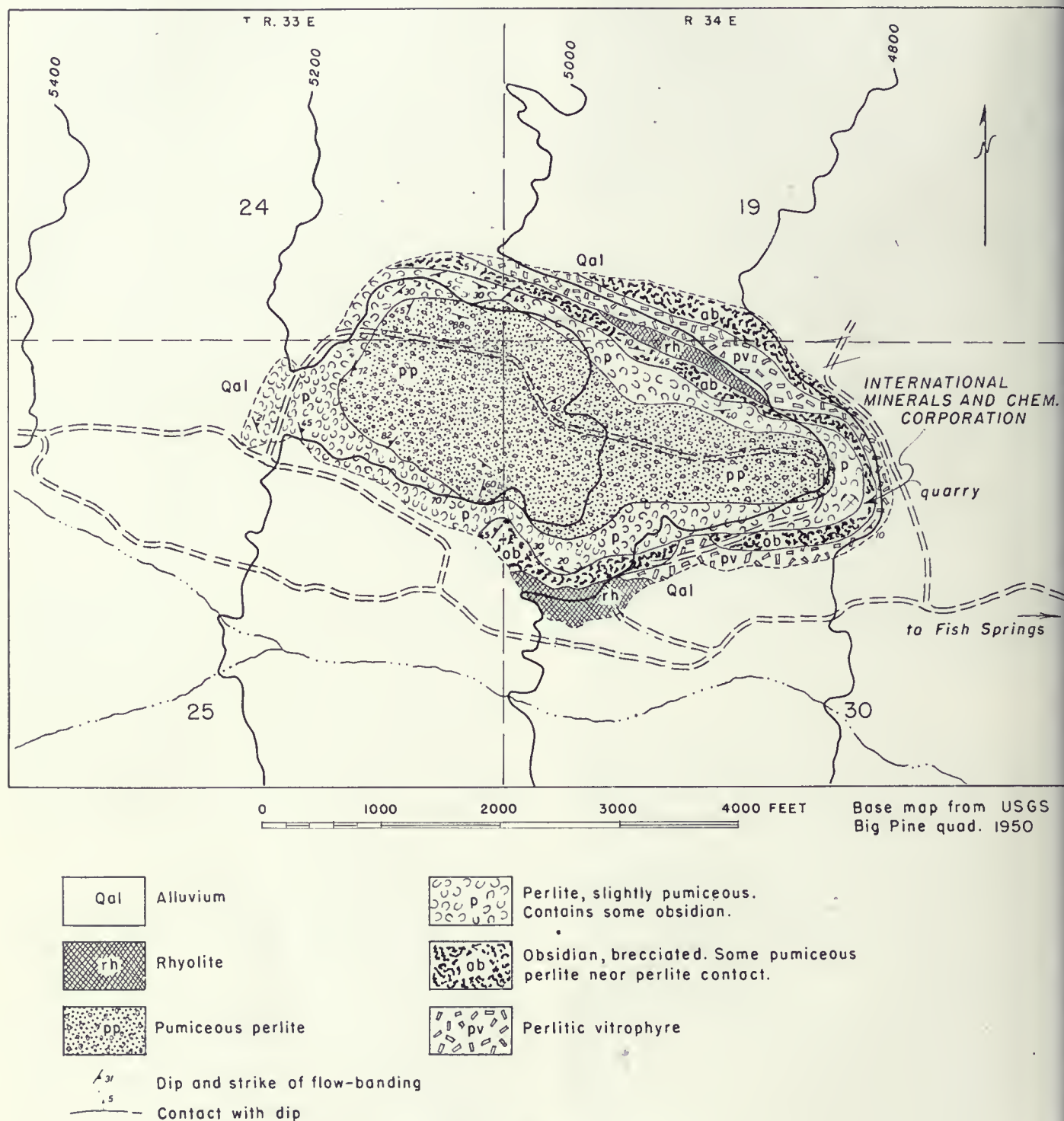


FIGURE 6. Geologic map of the Fish Springs perlite deposit, Inyo County.





FIGURE 7. Quarry at the International Minerals and Chemical Corporation's perlite deposit, Fish Springs perlite area, Inyo County. Scale is indicated by figure standing in front of the power shovel. The perlite is pumiceous, brecciated, and easily mined. Observer faces west, and the steep east-facing slope of the Sierra Nevada is visible in upper left-hand corner of the photograph.

eiated obsidian in a pumiceous perlite matrix, and by a dense, glassy perlitic-vitrophyre. The perlite is light-gray to white, medium to fine-grained, pumiceous, and contains local small rounded bodies of dark gray and black obsidian.

The perlite is mined by the International Minerals and Chemicals Corporation in an open cut high on the steep side of the dome. A bulldozer is used to remove the soft pumiceous overburden, and a small power shovel loads the perlite into trucks that haul it to a grinding and screening plant nearby. Perlite was first mined in the Fish Springs area in 1949, and has been continuously produced since then.

**Klondyke Area.** The Klondyke perlite area is in the Bristol Mountains, about 6 miles north of Klondyke, a siding on the Santa Fe Railroad, San Bernardino County. The perlite occurs in irregular to lenticular bodies and flows interbedded with tuffs, tuffaceous sediments, and flows of rhyolite. All are probably of late Tertiary age. The bodies of perlite range in thickness from a few feet to 50 feet and are as much as 1,000 feet in length. This sequence of volcanic rocks dips from 7 to 15 degrees southwestward. The perlite ranges from light- to dark-gray and locally shows reddish-brown streaks. Some of it is pumiceous and brecciated (Wright, et al, 1954, p. 188).

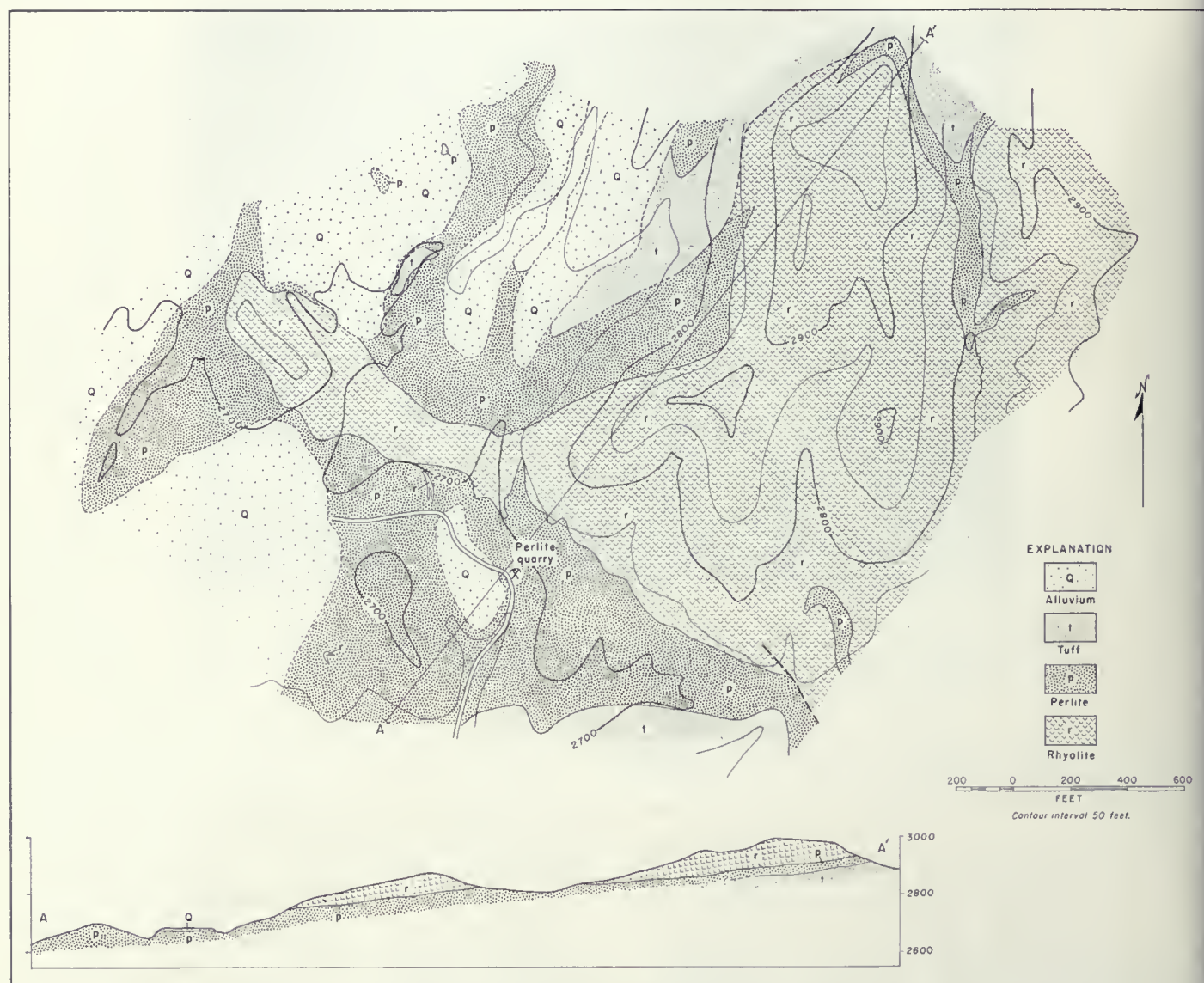
The American Perlite Corporation mines the perlite by open pit methods. Blasting is required to break the perlite which is then loaded into trucks and hauled 6 miles to the crushing and screening plant at Klondyke siding. Although perlite for experimental purposes was first produced from the Klondyke deposits in 1948, commercial production began in 1952.

**St. Helena Perlite Area.** In an area about 3 miles southeast of St. Helena in Napa County, perlite occurs in late Tertiary flows which range in thickness from a few feet to several tens of feet. The flows lie upon tuffs and conglomerates, and are overlain by flows of light-gray, vesicular dacite. All are exposed in broad north-west-trending folds. Locally the overlying volcanic rocks have been eroded away and large bodies of perlite are now covered only by sandy soil. The perlite is dark-gray to light-gray and contains unevenly distributed phenocrysts of feldspar, quartz, and hypersthene. Concentrations of these minerals locally constitute as much as 20 percent of the volume of the rock.

Perlite was discovered in the St. Helena area in 1947, and in 1949 small shipments were tested at a processing plant at Campbell, California. By 1951, the perlite was being produced on a commercial scale and two properties were in operation. One was developed as a source of perlite for processing plants in the San Francisco Bay; it became inactive in 1954. The other operation, Perlite Aggregates, Inc., which supplies an expansion plant near the deposit, is still in operation. All mining has been by open pit methods. The perlite was being blasted from the quarry walls and hauled to a crushing and screening plant near the quarry.

**Castle Mountains Perlite.** Three operators, Lewis Cox, the MoreLite Minerals Corporation, and L. S. Whaley Lumber Company, have mined perlite in the northern part of the Castle Mountains, eastern San Bernardino County. The perlite occurs largely in a zone exposed low on the north slope of Hart Peak extending for at least 3,000 feet along the northeast flank of the peak. The zone is a part of a thick section of Tertiary





GEOLOGIC MAP OF THE KLONDYKE PERLITE AREA, BRISTOL MOUNTAINS, SAN BERNARDINO COUNTY, CALIFORNIA

FIGURE 8.

acidic volcanic rocks that underlies all of the Castle Mountains. Although much of the zone is covered by a mantle of talus, individual perlite bodies of commercial interest are about 50 feet in maximum thickness and as much as several hundred feet long. The perlite zone strikes northeast and dips moderately northwest. Both pumiceous and nonpumiceous perlites are present and of commercial value. Locally the perlite contains spheroidal masses of rhyolite and veinlets of chalcedony. The reserves of perlite in these deposits appear to be large. The perlite is mined in quarries where perlite broken from the quarry walls by blasting is loaded into trucks by tractor loaders (Wright, et al., 1953).

*Miscellaneous Perlite Deposits in California.* Perlite also has been produced from several other deposits scattered throughout California. A deposit near Shoshone, Inyo County, has yielded a few hundred tons for experimental purposes. Several hundred tons of perlite from

deposits in the El Paso Mountains, eastern Kern County, were mined for test purposes and were found to be acceptable for the manufacture of expanded perlite. Perlite deposits in the Turtle, the Van Winkle, and Newberry Mountains, all in central and eastern San Bernardino County, are extensive and contain large reserves of expansible perlite rock. Large deposits of expansible perlite also exist in the Little Chuckwalla Mountains, eastern Riverside County.

Perlite deposits in the Warner Mountains, near Davis Creek, Modoc County, are among the first to be explored and mined in California. These too contain large reserves of expansible perlite, but their remoteness from processing plants and markets has retarded their development.

In addition to the above-listed deposits of perlite, others are scattered throughout California. Many of them are either too inaccessible or too small in size to be developed commercially. Many of the larger deposits,



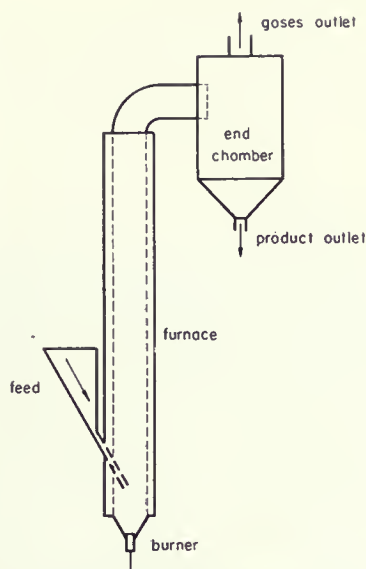


FIGURE 9. Vertical perlite processing furnace (Stein and Murdock, 1955, p. 12).

although readily accessible and suited to cheap mining methods, consist of perlite rock that is not suited to present methods of processing.

#### MINING AND PROCESSING OF PERLITE

As perlite is a low-cost commodity it must be mined by open pit methods. The perlite is broken by blasting

and the broken rock is loaded into trucks by bulldozer or power shovel and transported to crushing and screening plants commonly situated near the quarry.

The preparation of perlite for use as an aggregate or for other purposes involves essentially (1) the crushing of the perlite rock, (2) carefully sizing it and (3) expanding the sized material in a furnace. The success of a given processing plant depends upon several factors of which the more important are: (1) character of the perlite rock, (2) temperature at which the perlite expands, (3) extent to which water vapor has been driven out of the perlite particles before the softening point is reached, and (4) size distribution of the perlite fed into the furnace (Stein and Murdock, 1955, p. 105). In general three types of furnaces are used to expand perlite. They are the horizontal stationary furnace, the cocurrent rotary furnace, and the vertical furnace. Gas is the most commonly used fuel in each type. In the eastern part of the United States where low-cost gas is unavailable, the furnaces are oil-fired.

In processing perlite, the sized perlite rock is fed into the furnace, heated to temperatures of 1800° to 2000° F., and ejected within a few seconds. The hot, expanded perlite is collected in an end-chamber which feeds the hot perlite into a collecting system consisting of a bank of cyclones. In the cyclones the perlite is cooled and separated into the various size fractions and bagged. The vertical furnace is in common use throughout the United States. Expanded perlites ordinarily weigh from 3 to 20 pounds per cubic feet or from  $\frac{1}{30}$  to  $\frac{1}{4}$  the density of the sized, unfired material.



FIGURE 10. Interior view of vertical perlite processing plant operated by Panacalite Pacific, Inc., Los Angeles. Photo by Alexander Commercial Photo Service, Los Angeles.



### UTILIZATION OF PUMICE, PUMICITE, VOLCANIC CINDERS AND PERLITE

Of the 71,000 short tons of pumice produced in California in 1955, approximately 92 percent or 65,320 short tons were used as aggregate in concrete, 4 percent or 2,840 short tons for abrasive, 3 percent or 2,130 short tons for miscellaneous uses such as filtering, road surfacing and ice control, absorbents, and soil conditioners, and one percent or 710 short tons for acoustical and insulating plaster aggregate.

Concrete that contains a pumice aggregate ordinarily weighs from 60 to 80 pounds per cubic foot, whereas conventional concrete made of sand and gravel weighs from 140 to 150 pounds per cubic foot. Other advantages to pumice concrete over conventional concrete are (1) improved heat and sound insulation, (2) more fire resistance and can withstand a much wider temperature range without disintegrating, (3) ability to be sawed and nailed, and (4) greater freeze and thaw resistance (Chandler, 1955, p. 3).

The pumice used as an abrasive is produced in ground and block form. Pumice is valued as abrasive because, if pure, it consists of angular and sized fragments of uniform hardness. Only the purest grades are used as abrasives, and these must be free from all materials harder than glass. Only a very small part of the pumice is pure enough for use as an abrasive. Ground pumice is used as an abrasive agent in tooth paste, metal polishes, hand soaps, rubber erasers, and in the abrading and polishing of hard rubber and fiber board. The pumice used in metal polishes and tooth paste is ground to the finest particle size, usually minus 140 to 200 mesh. That used in finishing woodwork ranges in size from minus 80 to minus 100 mesh. Pumice scouring bricks and grill cleaners are cut from lump pumice which has uniform texture and hardness, and is devoid of hard, dense, glassy bands. Two sizes of bricks are produced, 3" x 3" x 6" and 4" x 4" x 8". Saw cuttings and pumice dust are collected and marketed as abrasive pumice. Reject and scrap pumice is stockpiled near the plant, and a limited amount of this material is shipped east where it is ground and marketed as an abrasive.

Some pumice has been used as a soil conditioner and in hydroponics. As a soil conditioner the functions of the pumice are to render the soil more porous and arable. In hydroponics the pumice, because of its absorptive nature, acts as a medium through which the plants grow and from which they extract the required chemical and moisture for growth.

Most of the pumicite mined in California is consumed by the agricultural industry where the pumicite is used as an insecticide and pesticide carrier. Pumicites, in general, have pH values ranging from 5.4 to 8.9, and form a suitable diluent for such active poisons as DDT, rotenone, pyrethrum, cryolite, nicotine, sulfur, and arsenates; all very effective in combating and destroying chewing insects (Moretti, 1947). The specifications for insecticide carriers are rigid. For pumicite, the dry screen analysis should be 90 to 99 percent passing 325 mesh. Average particle size as well as the range of particle size is closely controlled. The bulk density in the range of 35 to 45 pounds per cubic foot for ground dusting carriers and at about 60 pounds per cubic foot for airplane dusting carriers.

Both pumicite and ground pumice are used as admixes in the manufacture of cement. Cements that contain either pumice or pumicite resist the corrosive action of sea water, and are therefore extremely useful in the construction of salt water concrete structures. In recent years, pumicite has received considerable attention as a ceramic raw material because (1) it is a low-cost material, (2) requires little or no grinding to prepare it for use, and (3) imparts the ceramic bodies a toughness and freedom from warpage over wide firing ranges (Ceramic Industry, 1953, p. 134). Pumicite can be used in glazes, glass, enamels, and in the bodies of sewer pipe and other forms of pottery. When used in glazes, it is roughly equivalent to a material composed of 70 percent orthoclase and 30 percent flint. As most pumicite contains small amounts of iron, the use of pumicite is restricted to colored glasses, fiber glass, and ceramic bodies that need not be white.

About 80 percent of the perlite produced and expanded in California is used as aggregate in plaster. In this use it replaces sand and makes a plaster that is lightweight, has good acoustic and thermal insulating properties, is fireproof, resilient, nailable, sawable, and has good bonding properties. Perlite has been used as aggregate in concrete for roof decks, beams, building blocks, prefabricated units, and floors. Its relatively low compressive strength, however, has generally prevented its use in blocks, bricks, beams, and stress-bearing monolithic walls. Perlite also is used as a loose-fill insulation between wall studs, around steam pipes, in refrigeration ears, and deep freezers. It also is employed as loose-fill medium for imbedding hot-steel ingots during shipping. As a constituent of foundry sand, perlite improves the casting properties of the sand and prevents excessively rapid cooling of the mold.

Fines obtained during the processing of perlite are being employed as fillers in rubber goods, cleansing compounds, paints, glazed building tile, sandwich boards, metal-surface plaster, porous supports for catalysts and chemicals in gaseous reactions, in refractory brick, for filtering fruit juices, dry-cleaning compounds, alcoholic beverages, and other chemicals (North, 1955, p. 4).

Of the 708,481 short tons of volcanic cinders produced in California in 1955, about 85 percent were consumed by railroads as ballast and bank-widening. The remaining 15 percent was used as aggregate in concrete building blocks, in stucco, roofing granules, decorative stone in gardens, as a conditioner for soils, and in highway construction. Concrete aggregate material, commonly in the size range from minus 5/16-inch to 12 mesh, is shipped directly to the consumer either by rail or truck. Roofing granules, for use in built up asphalt-based roofs, are sold in bulk in car or truckload lots; some are later sacked by distributors for sale. Material smaller than 12-mesh is sold for agricultural use. Its action is to hold the soil and keep it friable; little or no nutritive value is claimed for the volcanic cinders.

### MARKETING

Most of the pumice, pumicite, and volcanic cinder mines in California are operated by firms that also operate processing plants and sell the products directly to the consumer or to contractors and distributors. As such firms ordinarily do not purchase crude material, no





FIGURE 11. Oblique aerial view of the southern Coso Range, Inyo County, showing pumice pits of the Crownite Corporation, 1—Ray Gill #31, 2—Ray Gill #13, and 3—Ray Gill #7, and the general geology in which plio-Pleistocene volcanic rocks consisting of flows and cinder cones of basalt (B), domes of perlite (in part obsidian) (P), and layers of lacustrine sedimentary rocks including pumice tuffs (Ls) rest upon a deeply eroded basement of pre-Cretaceous granitic and metamorphic rocks (Br). The pumice tuffs in the lacustrine sedimentary rocks represent the earliest periods of volcanic activity. The perlite was emplaced at a much later date as volcanic plugs, and the basalt flows and cinder cones probably represent a more recent volcanic activity. Alluvium (Qal) covers much of the geology and fills shallow, broad valleys. Observer faces northeast. Photograph courtesy of White's Studio, North Hollywood, California. Reprinted from *Division of Mines Bulletin 174*, fig. 73.



ready market exists in California for untreated pumice, pumicite and volcanic cinders. On the other hand, most of the perlite quarried in California is sold by the mine operators to other concerns which expand it and market the finished product. Of the three concerns mining perlite in California, two process their own rock as well as supply the market with graded perlite ore, and the third prepares the perlite only for other expanding firms. No perlite is sold in California in the crude, ungraded form. The independent owner of a deposit of any of these volcanic materials, in order to realize a profit from his holdings, usually must either lease or sell his deposit or attempt to mine and process and market the materials himself.

The mining of all of these volcanic materials is a field that has developed largely by rather small operations that have required much smaller capital investments than those of most other mineral commodities. In 1955, thirty-six operations existed in California whereas there were 17 in 1945. The field is highly competitive and many operations have been short-lived because competitive operations nearer markets were developed.

In 1956, California pumice for aggregate purposes was valued from \$2.00 to \$6.00 per short ton at the plant. Pumice specialty products including acoustical granules, have demanded high prices and the cost at the plant ranges from \$15.00 to \$30.00 per ton bagged. Pumice for use as acoustical plaster aggregate sold for \$24.00 to \$31.00 per ton at the plant. Since 1945, the pumicite used as diluent and insecticide carrier has consistently sold within the range of \$15.00 to \$20.00 per ton in carload lots at the plant.

In 1956, ground perlite rock ready for expansion sold at the plant for about \$6.00 per short ton. Expanded perlite, on the other hand, claims a much higher price and in 1954 was valued at \$43.00 per short ton at the expanding plant. Expanded perlite is packaged in 4-cubic foot multi-wall paper bags and shipped in truck or carload lots to the distributor or contractor.

In 1956, volcanic cinders for use as railroad ballast and highway construction were valued from \$0.18 to \$1.71 per ton at the mine. Cinders used for concrete aggregate were valued from \$0.50 to \$2.10 per short ton, and cinders used as roofing granules were valued at \$3.00 to \$5.00 per short ton in bulk, f.o.b. the plant.

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## PYRITES

By CHARLES W. CHESTERMAN

For many years, California has been one of the eight principal pyrite-producing states and in 1952 ranked the fourth in pyrite production. The chief use of pyrites is in the manufacture of sulfuric acid, which is being used in oil refining, the chemical industries, and manufacture of fertilizer.

**Mineralogy and Geology.** Pyrites is a general name applied to a group of iron-sulfide minerals including pyrite ( $\text{FeS}_2$ ), marcasite ( $\text{FeS}_2$ ), and pyrrhotite ( $\text{Fe}_{1-x}\text{S}$ , with  $x$  between 0 and 0.2) (Palache, et al., 1944, p. 223). Both pyrite and marcasite, when pure, contain 46.55 percent iron and 53.45 percent sulfur.

Pyrites, especially pyrite, are widespread in their occurrence. Pyrite is found as scattered grains in practically all types of rocks. It is most common as a gangue mineral in metallic ore deposits, but these are rarely mined for their pyrite. Only massive deposits of pyrite have been mined for their sulfur content.

Marcasite occurs under many of the same conditions as pyrite although it is not as common a mineral in metalliferous veins or crystalline rocks. Marcasite is easily decomposed and alters to brown limonite upon short exposure in a moist environment. As it does not occur in large masses, it has not been an important ore of sulfur. Pyrrhotite is commonly associated with chalcopyrite, pyrite, magnetite, pentlandite, and molybdenite. It commonly occurs in large masses or pipes of massive ore in such igneous rocks as gabbro, norite, or peridotite (as in the large nickeliferous pyrrhotite deposits at Sudbury, Ontario), or in metamorphic rocks with molybdenite, or in veins, or in pegmatites. Of these iron-sulfide minerals, pyrite has by far the greatest commercial importance.

In order for a sulfide deposit in California to be of commercial value for its sulfur content, the marketed ore generally should contain from 42 to 47 percent sulfur, although pyrite-bearing ore containing as little as 30 percent sulfur can be treated successfully (Fairlie, 1936, p. 74).

Most bodies of massive sulfides contain minor impurities such as arsenic, copper, silver, zinc, lime and magnesia, all of which render sulfur unavailable to the manufacture of sulfuric acid. This process, which is described in the sections on sulfur and sulfuric acid in this volume, involves the burning of pyrite and the liberation of sulfur dioxide gas. The zinc, copper, lime and magnesia combine with sulfur and oxygen to form sulfates thus causing the sulfur to remain in the cinder and unavailable. The arsenic in the sulfide ore is objectionable because of its corrosive effects on the lead walls in the chambers and flues of plants, and it lowers the quality of the sulfuric acid (Fairlie, 1936, p. 75).

Most of the world's pyrites output is mined in the United States, Australia, Canada, Cyprus, Japan, Norway, and Spain. The pyrites of commercial interest generally occur in lenticular to very irregular bodies enclosed in metasedimentary and/or meta-igneous rocks. They exist mostly as replacement deposits, and have sulfur contents in the general range of 35 to 50 percent. The largest deposits, including those in Spain, Australia,

and Cyprus contain ore that is measureable in millions of tons.

**California Deposits.** Most of the pyrite mined in California has come from bodies of massive sulfides in the West Shasta copper-zinc district, Shasta County. At least 13 mines in this district have contributed pyrite to the sulfuric acid industry, and all of them are in a northeast-trending belt, 10 miles long and 3 miles wide, about 15 miles northwest of Redding.

The massive sulfide deposits of the West Shasta district occur in a porphyritic facies of the Balaklala rhyolite (Devonian) which consists principally of silicic flows and interlayered pyroclastic rocks (figure 2). The sulfide ore bodies are lenticular in shape and range in size from a few thousand tons to more than 5,000,000 tons. Their distribution is controlled by folds and pre-mineral faults in the Balaklala rhyolite. Pyrite is the principal sulfide mineral in the ore bodies and most of them contain some copper, zinc and silver (Kinkel and Albers, 1951). The Iron Mountain mine of the Mountain Copper Company of California has been the principal source of pyrite in the West Shasta copper-zinc district and in California as well. At this mine, the pyrite is now removed by open-pit methods. At a mill near the mine the ore is crushed and screened for shipment to sulfuric acid manufacturers in the San Francisco Bay area (see sections on copper and zinc in this volume).

Mining in the West Shasta copper-zinc district dates back to the early 1860's when large outcrops of gossan on Iron Mountain were staked as iron ore. Silver was discovered in the gossan in 1879 and, at that time, a little interest was shown in the chalcopyrite and massive sulfides discovered during the prospecting for gold and silver. In 1895 a thorough prospecting of Iron Mountain indicated large bodies of copper-bearing sulfides, and in the same year the Mountain Copper Company, Ltd. acquired the property and began mining the massive sulfide ore for copper. By 1950, more than 6,000,000 tons of massive sulfide ore had been mined at Iron Mountain and at least 3,600,000 tons of pyrite were mined for use in the manufacture of sulfuric acid (Kinkel and Albers, 1951, p. 8).

Alameda County is probably the only other county in California from which pyrite has been produced commercially. Pyrite mining in Alameda County started about 1891 and continued almost uninterrupted into 1934. During this period of operation, the pyrite mines yielded a total production of over 250,000 tons of pyrite which averaged about 46 percent sulfur, 40 percent iron, 2 to 3 percent copper, and about \$2.00 per ton of gold.

The pyrite deposits in Alameda County occur in the Leona rhyolite (Plio-Pleistocene in age) which crops out as a narrow, discontinuous belt along the west flank of the Berkeley Hills from Berkeley southward to Decoto. The Leona rhyolite is both intrusive and extrusive in character. The pyrite ore bodies consist of a series of irregular lenses of massive sulfide composed principally of pyrite with minor amounts of chalcopyrite, chalcocite, bornite, and sphalerite. Several secondary minerals such as blue pisanite, greenish-blue chalcantite and pale



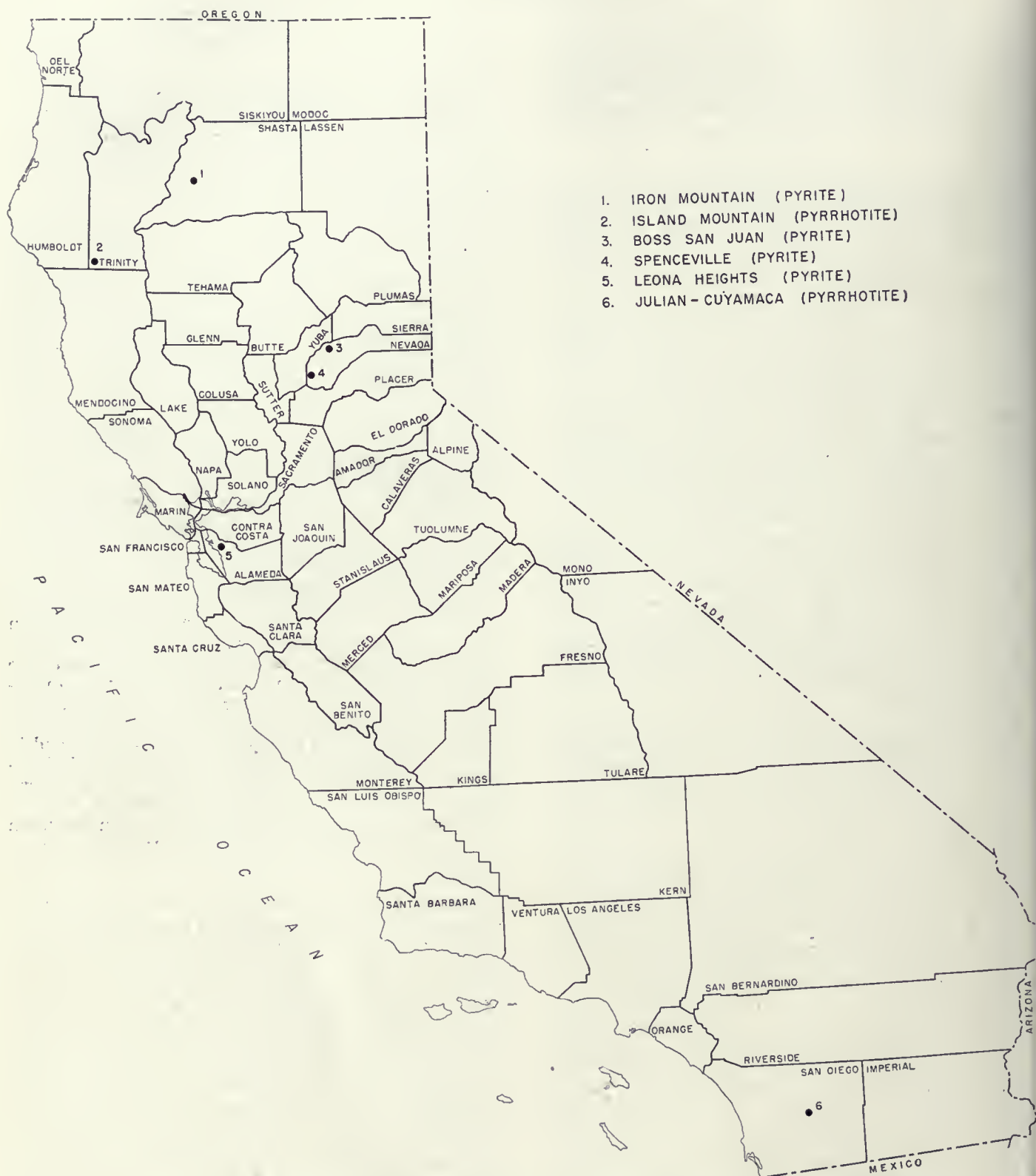


FIGURE 1. Index map of California showing location of principal pyrite- and pyrrhotite-producing areas.



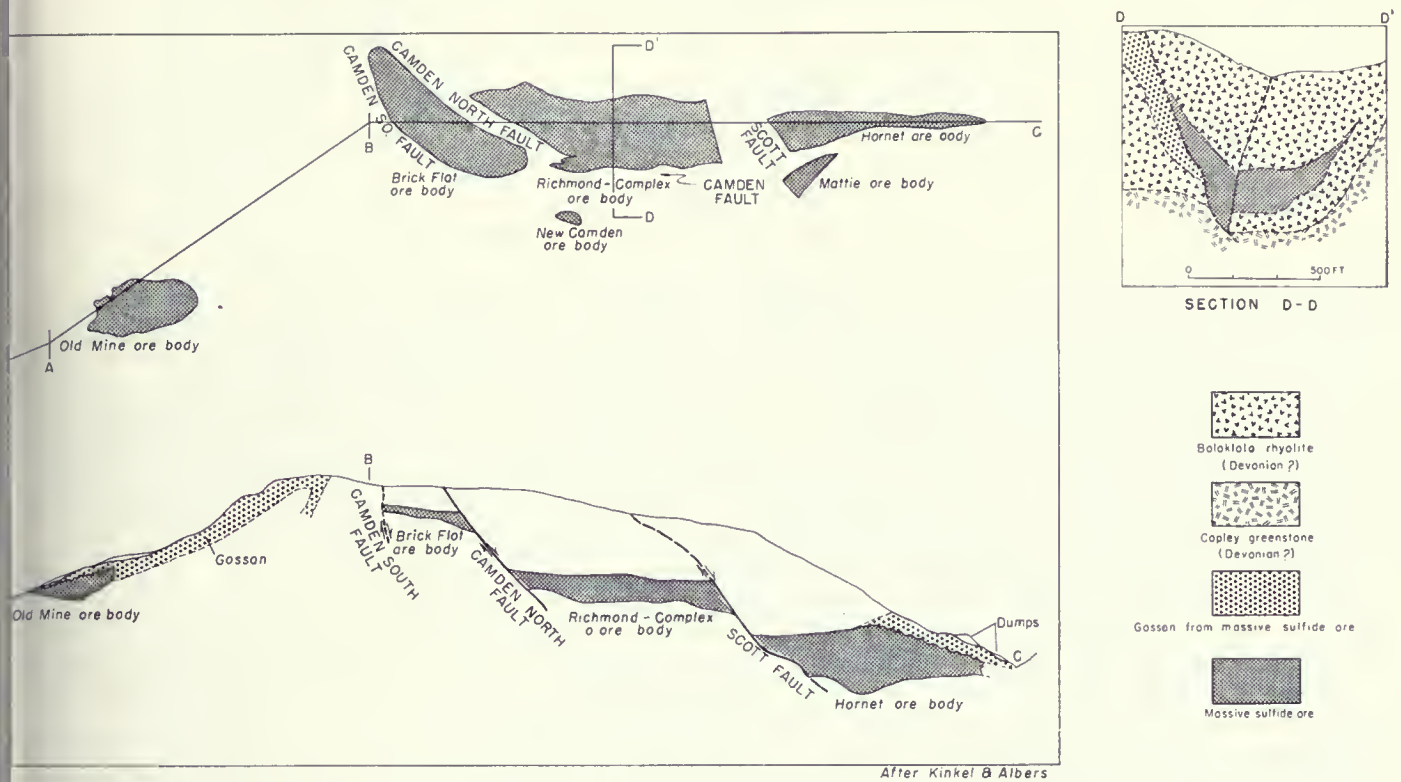


FIGURE 2. Map of the Iron Mountain mine, West Shasta copper-zinc district, Shasta County, showing mines plan, and longitudinal and cross-sections of massive sulfide ore bodies. (After Kinkel and Albers, 1951.)

green melanterite are present in the oxidized portions of the ore bodies and in the mine workings.

Two commercial pyrite mines, the Alma and the Leona, were developed in the area (Davis, 1950, p. 306). The Alma mine was developed by more than 5,000 feet of tunnels and drifts and was operated almost continuously from 1891 to 1920 by the Stauffer Chemical Company. The pyrite was used in the manufacture of sulfuric acid. The sinter, following roasting, was leached to recover the copper and silver content. The Leona mine was developed by more than 3,000 feet of workings (Huguenin and Castello, 1920, p. 33) and was in almost continuous operation from 1895 to 1934 when it was permanently closed. The Leona Mining Company worked the mine and sold pyrite ore to the Stauffer Chemical Company for manufacture of sulfuric acid (Davis, 1950, p. 306).

Although none of the mines in the foothill belt of the Sierra Nevada have been mined exclusively for pyrite, a few mines, especially the copper mines, have yielded pyrite as a by-product. The Spenceville copper mine at Spenceville, Nevada County, is credited with being the first mine in the state to yield pyrite for the manufacture of sulfuric acid. The Spenceville copper mine was opened early in the 1860's and was in almost continuous operation to about 1900. During this period, it produced 150,000 tons of ore averaging about 5 percent copper and between \$3.50 and \$4.50 per ton in gold and silver. The ore, consisting largely of pyrite, some chalcopyrite and a trace of gold and silver, occurs in a series of veins near the contact of diorite and granodiorite. Most of the mining was done in the main footwall vein which

measured 300 feet in length, 15 to 55 feet wide, and mined to a depth of 150 feet (Aubury, 1905, p. 164). The shaft is reported to have bottomed in massive pyritic sulfides.

The Boss San Juan mine, about 13 miles northeast of Nevada City, Nevada County, also contains sizeable bodies of massive sulfides. The ore consists of lenticular bodies of pyrite in foliated greenstones of the Calaveras formation. The pyrite lenses dip steeply from 70 to 80 degrees and are parallel to the foliation of the greenstone. The lenses range in length from 200 to 600 feet, 20 to 100 feet in width and have been prospected to about 400 feet in depth. The ore consists largely of pyrite, some quartz, 0.3 to 0.6 ounce gold per ton and averages about 4 percent copper. Mining and exploration has outlined an area about 4,000 feet long, 500 feet wide and 400 feet deep which appears to contain most of the pyrite lenses (Frederick, F. H., 1956, personal communication) and which are estimated to contain in excess of 3,000,000 tons of pyrite at 40 percent sulfur. By selective mining and/or beneficiation of the pyrite, the ore could be upgraded to 50 percent sulfur.

Massive sulfide bodies composed essentially of pyrrhotite with minor amounts of chalcopyrite and pyrite occur in Orange, San Diego and Trinity Counties. At the Friday mine in the Julian mining district, San Diego County, an irregular mass of nickel-bearing pyrrhotite is at the contact between gabbro and fine-grained mica schist. This deposit (figure 3) has been developed to a depth of 180 feet and contains on the average of 2.0 percent nickel, from 0.5 to 1.0 percent copper and may be a potential source of sulfur (Creasey, 1946, pp. 25-27).



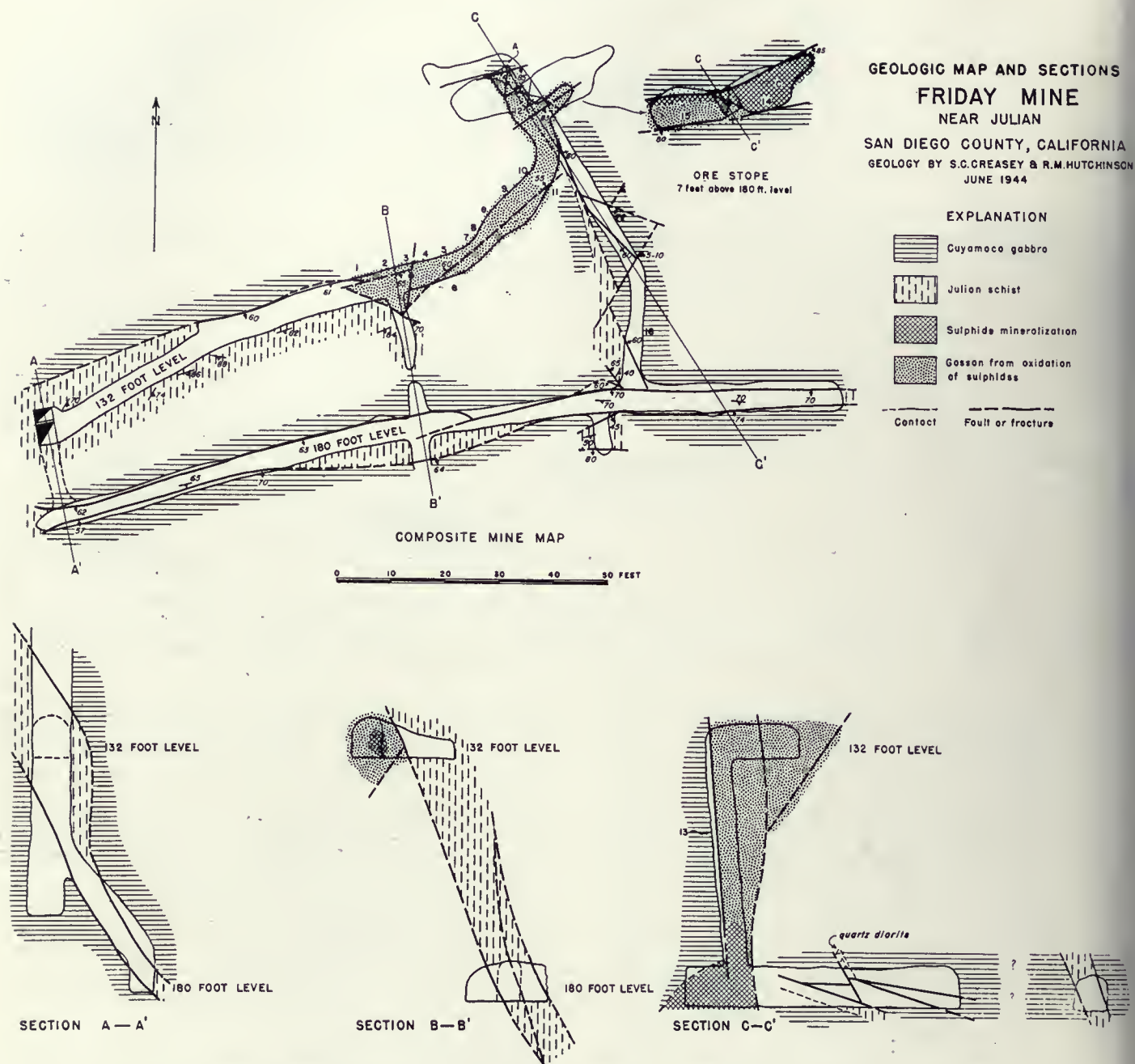


FIGURE 3. Geologic map and sections of the Friday mine, near Julian, San Diego County. (After Creasey, 1946.)

A large body of massive sulfide occurs at Island Mountain on the Eel River, northwest Trinity County. This deposit, which contains pyrrhotite as the only significant ore mineral, is an irregular body in sedimentary rocks of the Franciscan (Jurassic-Cretaceous) formation. The ore mined to date has averaged about 3.5 percent copper, 1.5 ounces silver and \$2.00 gold per ton of sulfides. Minor amounts of nickel and zinc are also present (Stinson, 1955). The pyrrhotite ore, measuring about 160,000 tons, was shipped to a copper smelter at Tacoma, Washington and used as a flux in the smelting of copper ores. The mine was in continuous operation for 12 years and was closed down in 1930.

In general, such ore is not considered to be a potential source of sulfur, as pyrrhotite contains no more than 39.2 percent sulfur which, moreover, is difficult to recover.

*Utilization.* For many years, pyrites have been a source of raw material for the manufacture of sulfuric acid (see section on sulfur and sulfuric acid in this volume) which is used extensively in the chemical industry, in oil refining, in the manufacture of fertilizers, and in the food processing industry.

Prior to 1920, the bulk of the sulfuric acid manufactured and consumed in the United States was made





FIGURE 4. Mining pyrite by open pit mining methods at the Iron Mountain mine of the Mountain Copper Company, Shasta County, California.



from the roasting of pyrites. With the successful development of the Frasch process of sulfur mining, the pyrite industry has languished because of the preference of acid manufacturers for elemental sulfur. In spite of the increases in production of the Frasch sulfur, pyrites are still being imported into the United States, from Australia, Canada, Cyprus, Portugal and Spain through customs districts in the eastern United States. Most of the sulfuric acid produced from the pyrites mined in Shasta County is consumed by industries in the San Francisco Bay area.

*Specifications and Prices.* Specifications for pyrite are usually determined by agreement under contract between the producer and the consumer. As pyrite ore is valuable only for its content of available sulfur, the ore should contain only minor amounts of copper, zinc, lead, antimony, calcium, magnesium, fluorine and chlorine. For each percent of copper in an ore, there will remain in the cinder 0.05 percent sulfur; of zinc, 0.5 percent sulfur; of lead, 0.15 percent sulfur; of lime (CaO), 0.57 percent sulfur; and of magnesium (MgO), 0.80 percent sulfur (Fairlie, 1936, p. 75). For example, an ore that assays 44 percent sulfur, but also contains 3 percent zinc, 2 percent copper and 0.5 percent lime, could contain 41.22 percent available sulfur. This is, however, based upon the assumption that all of the sulfur is converted into sulfates, and this is rarely true. Ores were formerly classed as lump and fines. Lump ore ranged in size from 2 to 10 inches and was supposed to contain not more than 10 percent minus  $\frac{1}{2}$ - or  $\frac{3}{8}$ -inch screens. However, with the development of new roasting equipment and techniques, it is now possible to utilize the smaller sizes successfully.

The pyrite ore shipped to sulfuric acid manufacturers in the San Francisco Bay area from the deposits of the Mountain Copper Company of California in Shasta County is all crushed to minus  $\frac{3}{8}$ -inch mesh.

The present (1956) market for pyrites in California is limited to two sulfuric acid manufacturers.

The average value for all domestic pyrite in 1955 was \$6.00 per long ton. In March, 1956, Canadian pyrites, f.o.b. works, per long ton, sold for \$3.00 to \$5.00, and domestic pyrites at the consumer's plant, per long ton, sold for \$9.00 to \$11.00 (Oil, Paint and Drug Reporter). California pyrites in 1956 sold in the general price range of \$11.00 to \$15.00 per short ton, f.o.b. the mine.

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## PYROPHYLLITE

BY LAUREN A. WRIGHT

The commercial mining of pyrophyllite in California began in 1945, and through 1956 had produced an estimated 85,000 tons of the mineral. Most of this output has been obtained from a single quarry in pre-Cretaceous metamorphic rocks of the White Mountains in Mono County. The remainder has been mined in smaller operations in Mono, Inyo, San Bernardino, and San Diego Counties. In 1956, California ranked second to North Carolina as a domestic source of pyrophyllite. The pyrophyllite produced in California has been used as an insecticide carrier and, less abundantly, as a paint extender, ceramic raw material, and filler.

*Mineralogy and Geologic Occurrence.* Pyrophyllite ( $\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2$ ) closely resembles talc in appearance and physical properties and the two minerals are used similarly (see section on talc in this volume). As pyrophyllite contains aluminum instead of magnesium, it is best distinguished from talc by a positive test for aluminum. It is distinguished from most other minerals by its softness (1 to 2 on Mohs' scale) and by a micaceous habit. Some pyrophyllite, however, is massive and some occurs as clusters of radiating needles. The pyrophyllite of commerce generally is a schistose rock that consists of a fine-grained mixture composed mostly of the mineral pyrophyllite and containing quartz and sericite as the most abundant, but not necessarily deleterious, impurities.

Most pyrophyllite deposits of commercial interest are hydrothermal alterations of acidic volcanic rocks. Such large-scale pyrophyllitization ordinarily has involved the introduction of aluminum and commonly has been preceded or accompanied by silicification.

The best known and most extensively worked pyrophyllite deposits in the United States are in North Carolina. Here lenses of pyrophyllite, as much as 1500 feet long and 500 feet wide (Burgess, 1949, p. 757) occur in a series of tightly folded and metamorphosed volcanic and sedimentary rocks. The alteration appears to have been the most intense in shear zones localized in the more siliceous of the volcanic rocks (Stuckey, 1925). For many years these deposits have contributed most of the pyrophyllite that is mined and consumed in the United States.

*Localities in California.* All but a very small part of the pyrophyllite mined in California to date has been obtained from three relatively small areas—one in southeastern Mono County, another in west-central San Bernardino County, and the third in west-central San Diego County. A deposit near Fish Springs, Inyo County, also has been worked. Excellent specimens of radiated pyrophyllite have been found in the western foothills of the Sierra Nevada, but the mineral has not been mined commercially in this area.

The pyrophyllite deposits of Mono County lie low along the west face of the White Mountains in the belt of pre-Cretaceous metamorphosed volcanic and sedimentary rocks that also contains the andalusite deposits described elsewhere in this volume. The most productive single source of pyrophyllite in this belt, and in Cali-

fornia as well, is the Pacific mine (fig. 2) about 16 miles north of Laws.

The Pacific mine appears to be on the largest of the pyrophyllite bodies that have been worked in California to date. The deposit trends northwestward and dips steeply southwestward, is about 200 feet wide, and apparently extends for at least several hundred feet in both directions beyond the limits of the present workings. It consists largely of schistose, very friable rock that is composed predominantly of pyrophyllite. Quartz-rich waste rock has been encountered in a layer 20 to 30 feet thick near the center of the body. Most of the pyrophyllite schist is iron-stained to shades of red, orange, or yellow. Some masses, however, are white or nearly so, and are mined selectively.

The Pacific deposit is owned and operated by Huntley Industrial Minerals, Inc. It has been developed by a single quarry (fig. 1) which has been in almost continuous operation since 1945. In 1956, the quarry consisted of several irregularly spaced benches, was about 150 feet in maximum width and about 100 feet in total height. The pyrophyllite is mined by means of a bulldozer and loader and is trucked to a mill at Laws.

The Colton property, about 2 miles south of the Pacific deposit and in the same pyrophyllite-bearing belt of metamorphic rocks, has been worked intermittently and on a smaller scale. It also is owned and operated by Huntley Industrial Minerals, Inc. Previous to 1955, the mining was confined to several small cuts near the floor of a canyon. Here a pyrophyllitic zone, although about 200 feet thick, is mixed with impure quartzite and cannot be mined extensively by open-cut methods. In 1955, another body was opened at a locality about half a mile southeast of the older workings and high on the south wall of the canyon. This body is about 100 feet in maximum thickness and is at least several hundred feet long. It is bordered by mica schist and quartzite and contains quartzite layers. The pyrophyllite is less friable and generally less discolored than that at the Pacific mine and the operators report that it is suitable for use as a ceramic material.

The Victorite pyrophyllite deposit (Wright, et al., 1953, pp. 243-244; and Bowen, 1954, pp. 158-160) about 12 miles northeast of Victorville, San Bernardino County, has been worked intermittently since 1950. It is presently (1957) operated by the Mineral Materials Company, Alhambra. The deposit consists of a steeply dipping zone in volcanic rocks of the Triassic (?) Side-winder series. The zone is about 1500 feet in exposed length and as much as 200 feet wide. It has formed by the hydrothermal alteration of the volcanic rocks and contains much material that is incompletely altered or too siliceous to be salable. Within the zone, however, are lenses several tens of feet wide that consists largely of pyrophyllite, and that can be mined by open pit methods.

The pyrophyllitic rock at the Victorite deposit is mostly schistose, but some is blocky. It ranges in color from white to pale gray and much of it is iron-stained. The quarried material has been stock-piled at the de-





FIGURE 1.

posit and shipped, as needed, to the Kennedy Minerals Company mill in Los Angeles.

The Pioneer pyrophyllite deposit (Jahns and Lance, 1950), in the San Dieguito area of west-central San Diego County, was most actively worked in the middle and late 1940's, and has been operated only at irregular intervals in later years. The pyrophyllite-bearing rocks occur within and are alterations of the Santiago Peak volcanics which are probably of Jurassic age. In the mine area, the volcanic rocks are mostly latitic to quartz dacitic in composition.

The pyrophyllitization has been guided mainly by fractures and shears and partly by differences in the original composition of the host rocks. It was preceded and accompanied by and marked silicification, so that silica is a widespread impurity. The pyrophyllite-bearing rocks occur in numerous lenticular bodies most of which consist of subcommercial material. All of the pyrophyllite mined to date has been from a single body 150 or more feet long and about 15 feet in average width. The commercial rock consists of a white to cream-

colored pyrophyllite schist whose fracture surfaces commonly are stained with iron and manganese oxides. Most of the mining was done by Pioneer Pyrophyllite Products of Chula Vista and the pyrophyllite was ground at a mill in Chula Vista.

Since 1954, small tonnages of talc have been mined from the Four Gee deposit, which is about one mile east of the Pioneer deposit and in a similar geological setting.

The pyrophyllite produced near Fish Springs in Inyo County was obtained from the Imus deposit in the period 1948-50. This deposit, which is about 5 miles north-northwest of Aberdeen, consists of a poorly exposed body of pyrophyllite schist which is overlain by crinoidal limestone. Its other exposures are overlapped by alluvium so that the size of the deposit is undetermined. The mined material was shipped to a mill at Zurich Siding, then operated by Blue Star Mines, Ltd.

*Mining Methods and Treatment.* All of the pyrophyllite produced in California has been mined by surface methods involving the use of bulldozers and small power



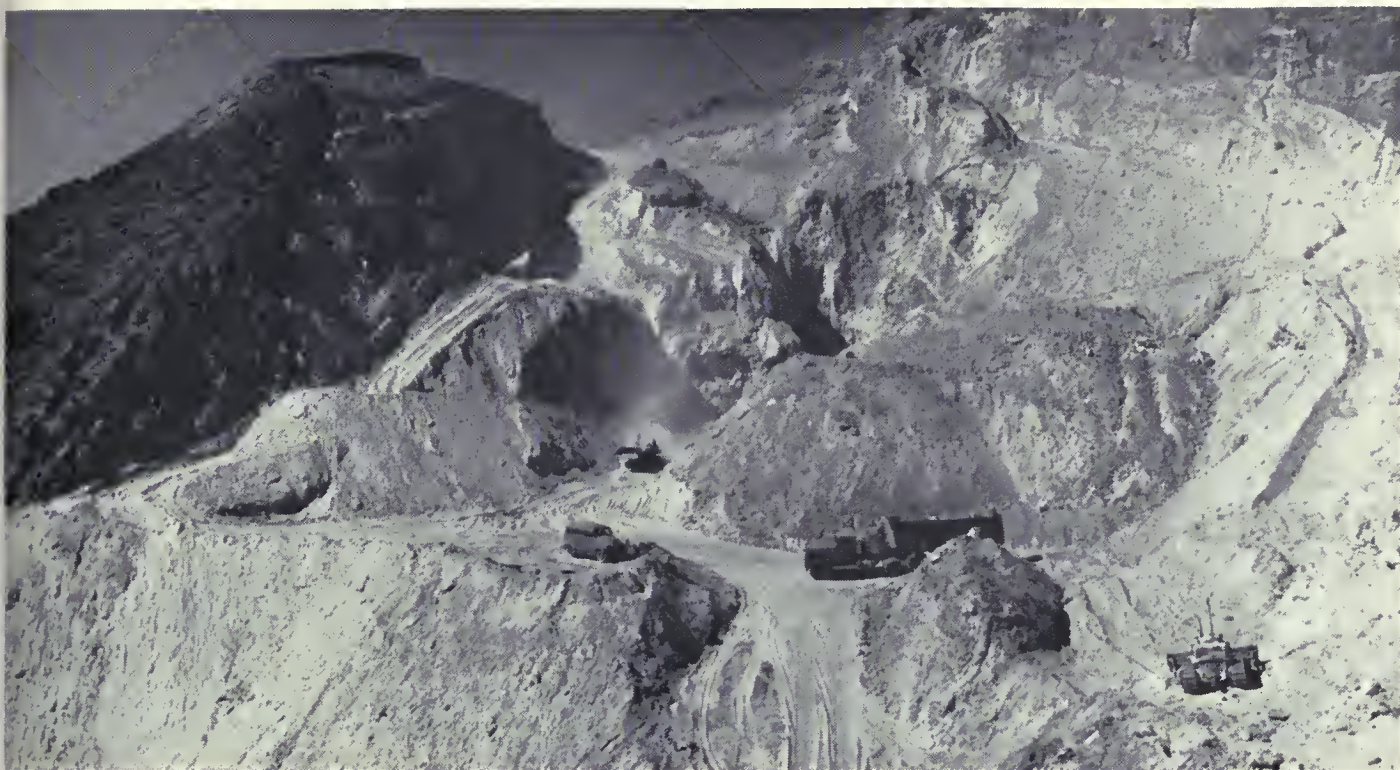


FIGURE 2. View north toward quarry at Pacific pyrophyllite deposit, Mono County. Deposit is part of steeply dipping series of pre-Cretaceous metamorphic rocks. Most of rock exposed in quarry is of commercial value.

shovels, or loaders. Little blasting has been required. In North Carolina, however, much of the pyrophyllite is removed by underground operations. The underground mining of off-color pyrophyllite in California would be hindered by the relatively low prices paid for the milled product and by the availability of similar, less expensively mined pyrophyllite.

In California, pyrophyllite is milled in the same equipment that is used to treat talc—Raymond roller mills in closed circuit with air separators (see figure in section on talc and soapstone in this volume). In North Carolina, conical pebble mills, as well as roller mills, are employed, as the pebble mills are well-suited to the preparation of pyrophyllite for ceramic use. The North Carolina mills yield several types of grinds ranging from minus 80 to minus 325 mesh. In California, where the use pattern for pyrophyllite has been somewhat limited, the material generally has been ground to about 95 percent minus 325 mesh.

**Utilization.** As pyrophyllite and talc have very similar physical properties, they are used similarly and are competitive commodities. The principal useful properties of pyrophyllite, as of talc, are a marked softness, a flaky to fibrous habit, good coverage, physical and chemical inertness, a high fusion point, low shrinkage and resistance to thermal shock when fired, good retention when used as a filler, and high absorption of certain oils and other liquids.

In 1955, the following use pattern pertained for the 155,000 tons of pyrophyllite that were mined in the United States: insecticides, 35 percent; ceramics, 25 percent; refractories, 15 percent; asphalt filler, 10 percent;

paint, 10 percent; rubber, 3 percent; and miscellaneous, 2 percent. (U. S. Bur. Mines, Mineral Market Rept., MMS No. 2567). Although the national consumption has risen steadily since pyrophyllite was first mined in the early 1920's, the use pattern has varied considerably, as to both tonnage and percentage. In recent years the tonnages used in insecticides, ceramics, paints, and refractories have risen, whereas the tonnages used in rubber have declined. Of the 15,000 to 20,000 tons of pyrophyllite now mined and consumed annually in California, an estimated 75 percent is used as a carrier for insecticides, 20 percent as an extender in paints, and 5 percent as an



FIGURE 3. View east toward Pioneer pyrophyllite deposit, San Diego County. Deposit is an alteration of Santiago Peak volcanics of Triassic age, which underlie most of the area shown.



ingredient in miscellaneous products, including ceramics and rubber.

The increased usage of pyrophyllite as a carrier of insecticides has come with the development of the technique of crop dusting from airplanes and the introduction of the DDT poisons with which pyrophyllite is particularly compatible. This market varies with the abundance of insect pests from year to year.

In the eastern United States, pyrophyllite competes on a virtually equal basis with talc as a ceramic raw material, particularly in the manufacture of wall tile. Most of the pyrophyllite that has been mined in California fires off-color and is unsuited to ceramic uses. In 1957, however, the operators of the Colton deposit in Mono County stated that increasing tonnages from this deposit were being employed in ceramics.

As material to be used as a paint extender must grind white, the run-of-mine pyrophyllite from the known deposits in California is generally unsuited to this use. Selectively mined pyrophyllite from the deposits in Mono County, however, is marketed as a paint extender.

*Marketing and Prices.* The problems of marketing pyrophyllite in California are essentially the same as those noted in the section on talc and soapstone in this

volume. In 1957, the various grades of pyrophyllite mined and milled in the state were being sold in the general range of \$15 to \$30 per ton ground and bagged in Los Angeles.

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## QUARTZ CRYSTAL

(Electronic Grade)

BY LAUREN A. WRIGHT

Quartz crystals are used in the manufacture of plates known as quartz crystal oscillators, whose piezoelectric properties permit a precise control of frequency in radio transmitters and other electronic equipment. Crystals suited to this application are uncommon and during World War II were in particularly high demand for use in portable military transmitters. Although adequate deposits of such crystals have been intensively sought in the United States, all but a small part of the domestic requirements have been imported from Brazil. During World War II, electronic-grade quartz crystal was obtained from gold-bearing placer deposits near Mokelumne Hill, Calaveras County, California. Synthetic quartz crystals can be manufactured, but to date, these are too expensive to be competitive with the natural material.

**Physical Properties and Geologic Occurrence.** Quartz ( $\text{SiO}_2$ ), one of the most abundant minerals in the earth's crust, enters into the mineral industry in various ways. It is, for example, a common constituent of many of the rocks that are quarried as crushed rock and dimension stone, and the principal constituent of most sand and gravel aggregate. Relatively pure quartz, in the form of silica sand, quartzite, or massive (vein and pegmatite) quartz, also has many commercial uses. All of these commodities are very abundant and are treated elsewhere in this volume.

The material known as quartz crystal, electronic (or radio) grade, however, is relatively rare. By definition, such crystals must be sufficiently large and unflawed to be fabricated for use in electronic equipment. Such use stems from the ability of a thin, crystallographically oriented wafer of quartz crystal, commonly known as an oscillator plate, to generate an electrical charge when pressure is applied to its surface, and to expand or contract in response to an electric current. This property, known as the piezoelectric effect, is most usefully applied to control frequency in electronic equipment, especially radar and radio transmitters.

To yield oscillator plates, quartz crystals generally must weigh at least 100 g., be at least 2 inches long parallel to the vertical axis, and at least 1 inch in diameter normal to the vertical axis, but when these are unavailable, somewhat smaller crystals are used. Although quartz crystals of suitable size are quite common throughout the world, most of them are rendered unusable by crystallographic imperfections, known as optical and electrical twinning, or by cracks, bubbles or inclusions. Although during World War II, certain slightly colored or clouded crystals were accepted, only colorless, perfectly transparent material was being used in 1956. Twinning in some specimens can be detected by irregularities on the crystal surfaces, and other imperfections also can be seen with the unaided eye; but most of the crystals that at first appear to be unflawed have invisible imperfections that can be detected only with the aid of laboratory equipment.

Most of the world's output and virtually all of the free world's supply of electronic grade quartz crystal is

mined in Brazil. The Brazilian deposits consist mostly of quartz veins in Paleozoic sedimentary rocks (Johnston and Butler, 1946, pp. 601-650). A small proportion of the Brazilian output is obtained from pegmatites and eluvial (residual) deposits. The veins are very numerous, consisting predominantly of bull quartz. They contain an extremely small proportion of electronic grade crystals which line cavities. The veins have been developed by hundreds of small mines, most of which were pressed into operation during World War II. Even the larger of these mines have averaged only about one ton of usable crystals for every 10,000 tons of material removed (Dietrich, 1956).

An insignificant fraction of the electronic grade quartz crystal that has been used in the United States has been mined from domestic sources. Of these, the most productive have been quartz veins in Ouachita Mountains of Arkansas (Engel, 1952). Here the quartz occurs as cavity fillings in veins that cut Paleozoic sedimentary rocks. A small production of usable crystals also has been obtained from North Carolina and Virginia as well as from California.

**California Localities\*.** In California, quartz crystals of radio grade have been found in the auriferous gravels and hydrothermal veins of the western foothills of the Sierra Nevada, and in pegmatites of the Peninsular Ranges. Most of the state's quartz crystal output has been obtained from auriferous gravels at Chili Gulch,  $2\frac{1}{2}$  miles south of Mokelumne Hill, Calaveras County (Durrell, 1944, pp. 423-433). Quartz crystal was first mined here in 1897, but the property probably was worked previously for gold. The early quartz crystal production, obtained in 1897-98, was used as ornamental

\* Most of the following information on quartz crystals in California was kindly supplied by Dr. Cordell Durrell, Professor of Geology, University of California at Los Angeles.

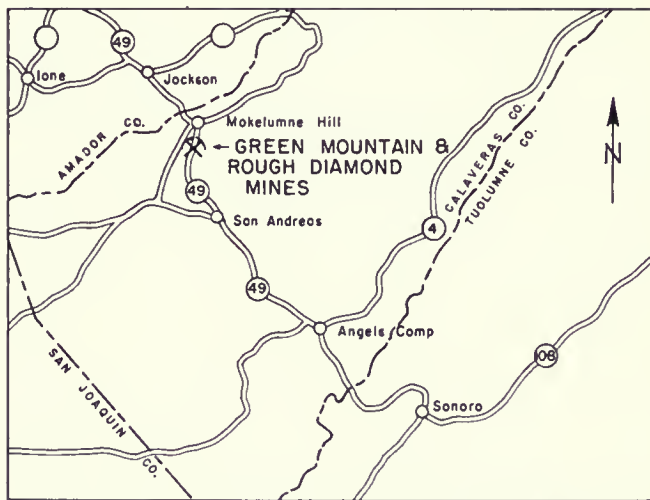


FIGURE 1. Index map showing location of Green Mountain and Rough Diamond mines which have yielded electronic grade quartz crystals.



material (Kunz, 1905, pp. 64-66). The property was reopened for a short period during World War I and the quartz crystal output was marketed "for scientific purposes" (Durrell, 1944, p. 423). Operations were resumed during the wartime period 1942-44, and the area yielded several thousand pounds of quartz crystal, but only a small fraction of this was of electronic grade.

The crystal-bearing gravels, which possibly are of upper Eocene age, fill a stream channel that has been cut in pre-Tertiary slate and greenstone. Most of the crystals were encountered within 6 feet of bedrock. The crystals occur both singly and in clusters and show a lack of wear which strongly suggests that they have been transported but a short distance from their bedrock source. None were found in place. Single crystals that weighed from 10 to 30 pounds each were common, and one is said to have weighed more than a ton.

The crystals have been removed from the underground workings of two old drift mines, the Green Mountain (Calaveras Crystal or McSorley) mine and the Rough Diamond mine. In 1944, the combined reserves of these properties were estimated (Durrell, 1944, pp. 432-433) at about 17,000 pounds of which approximately 5 percent would be of electronic grade. In 1950, however, the deposits were believed to have been nearly exhausted.

In 1943, a few crystals of electronic grade quartz were obtained from a small hydrothermal vein at the Mable H mine, 2 miles east of Camp Nelson, Tulare County. The crystals removed from this deposit have ranged from 1 inch to 3 inches in diameter, but most of them have contained bubbles.

The Senpe pegmatite near Pala, San Diego County, also yielded a small poundage of usable crystals during World War II (Jahns and Wright, 1951, p. 49). Large transparent quartz crystals have been removed from other pegmatites in San Diego and Riverside Counties, but abundant twinning generally has rendered the crystals non-electronic.

Elsewhere in California, possible sources of usable quartz crystal include a quartz vein in serpentine on the Gorman Ranch, three-quarters of a mile from Michigan Bluff, Placer County; placer deposits between Dry Creek and Indian Creek, northeast of Fiddletown, Amador County; gold-bearing quartz veins at Our Chance mine, 7 miles northeast of Mariposa, and at Giles Ranch near Hornitos, both in Mariposa County; and a pegmatite on the east of Greenhorn Mountain, 5 miles west of Kernville, Kern County. The Fiddletown deposits perhaps are the most promising of the known quartz crystal deposits in California, but none of these deposits appears to be capable of sustained production, except under conditions of unusual necessity.

*Classification, Processing, and Synthesis.* Quartz crystals of electronic quality are graded and classified as close to the deposits as possible in order to minimize the handling of non-usable material. The mine-run material is cleaned and trimmed, and the obviously subcommercial crystals are eliminated by a preliminary visual inspection. The remaining crystals are sorted according to size and the faced individuals are separated from the unfaced. All are immersed in an oil bath with the same refractive index as quartz. Here, optical twin-

ning can be detected in monochromatic polarized light, and minute fractures, bubbles, and inclusions become visible when illuminated with an arc lamp. A defect, known as electrical twinning and which also renders quartz crystals unusable for electronic purposes, cannot be detected by optical methods. Its presence can be determined by etch tests which ordinarily are applied by manufacturers after the crystals have been otherwise classified.

The National Stockpile Material Purchase Specifications, P-43 (1951), classify usable quartz crystals into 133 categories based on weight, percent of recoverable material, nature of defects, and whether faced or unfaced. Similar categories also form the basis for sales on the open market.

Manufacturing techniques are designed to recover the highest possible number of properly oriented oscillator plates per unit weight of crystal material. The plates are square, rectangular, or circular. They commonly are 1 millimeter or less thick and half to three-quarters of an inch in maximum dimension.

After determining the suitability of a crystal by means of oil bath and electric twinning tests, the manufacturer mounts it in a diamond saw so that the usable part of the crystal can be sliced into wafers along a plane that is properly oriented with respect to the crystallographic axes. The orientation of faceless specimens can be determined by special techniques. Blanks of the desired lateral dimensions are cut from the defect-free parts of the wafers, and the blanks are ground and polished by lapping to minus 0.0001 inch tolerances. They are then etched to remove the quartz dust and abrasions.

Oscillator plates are produced almost entirely by small concerns, and most of the plants are in the industrial areas where electronic equipment is manufactured. In 1954, ten plants in California were thus engaged (U. S. Bur. Mines, Mineral Market Report, MMS No. 2441). These plants, which are in both the Los Angeles and San Francisco Bay areas, produced about 5 percent of the 3.9 million piezoelectric units manufactured in the United States during that year, and in 1956 they were continuing at about the same rate.

Since the early 1940's, when the demand for electronic-grade quartz crystal became acute and the supply was uncertain, much research has been devoted to the synthesis of quartz crystals. By 1953, suitable crystals were being made by processes that involved hydrothermal synthesis in autoclaves at pressures of 7,500 to 15,000 psi and at temperatures of 350° to 410° C. (Walker, 1953). By 1956, however, such crystals could not yet be produced at costs competitive with the prices of the natural crystals.

*Utilization.* By definition, electronic-grade quartz crystal must be suited to the manufacture of piezoelectric units, and it is put almost wholly to this use. In 1954, about 96 percent of the units manufactured in the United States were oscillator plates for radio and radar equipment, 3.7 percent were telephone resonators, and the remainder were plates for miscellaneous electronic uses including filters and ultrasonic equipment (U. S. Bur. Mines Mineral Market Rept. MMS No. 2441). The units for each use are similar, but are cut some-



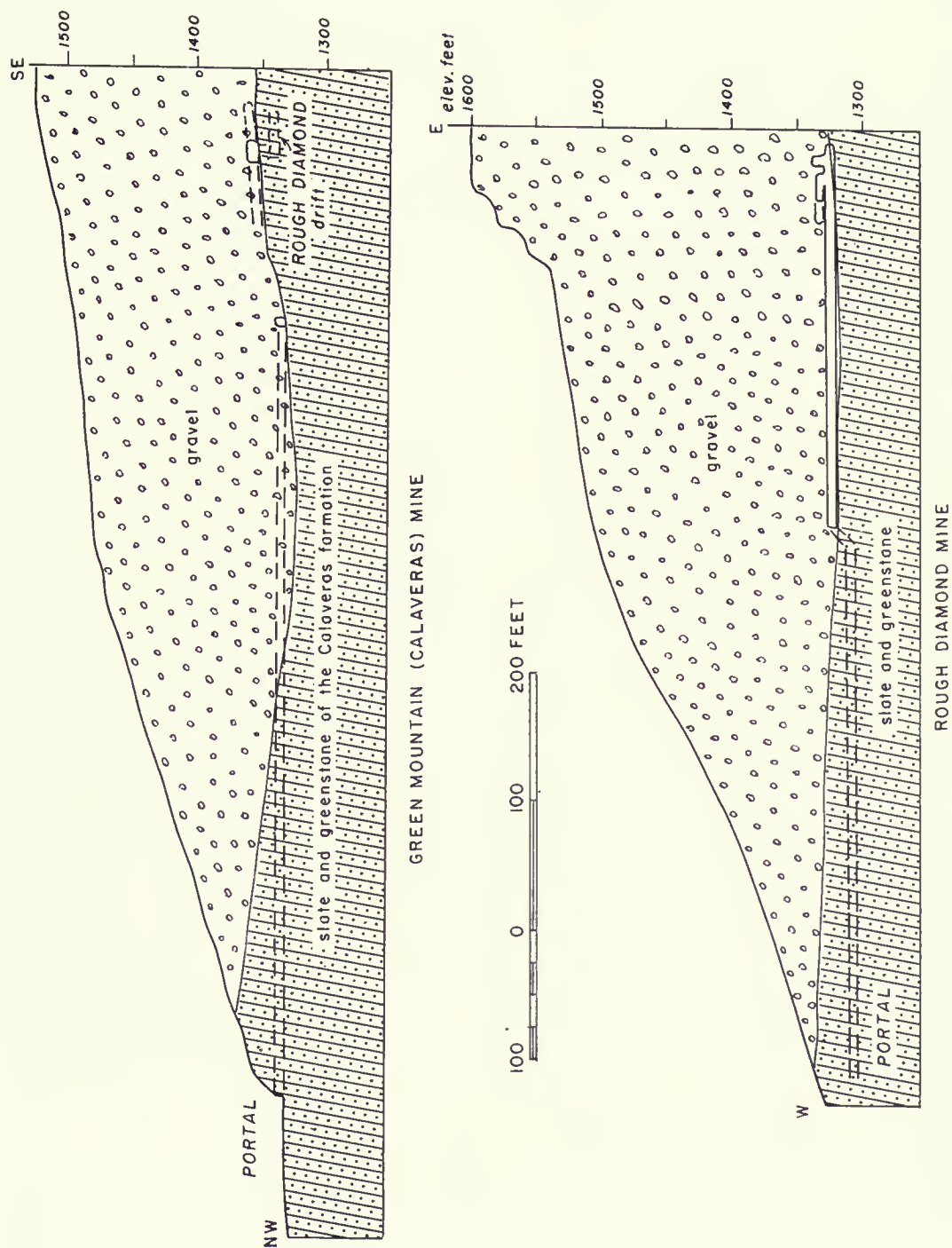


FIGURE 2. Cross sections through Green Mountain (Calaveras) and Rough Diamond quartz crystal mines, Calaveras County.  
*Modified after Thayer and Durrell, in Durrell, 1944.*



what differently. All types are manufactured in California.

Minor quantities of electronic-grade quartz are made into special optical objects such as prisms, lenses, and wedges. Some of it also is used as a semi-precious gem (see section on gem stones in this volume).

*Markets and Prices.* The sale of electronic-grade quartz crystals in the United States is handled almost entirely through brokers in New York City, who have obtained more than 95 percent of their stock from Brazil. Most of the manufacturers of piezoelectric units, including those in California, stand ready to purchase acceptable material from domestic producers, and indeed would welcome the development of such sources. In 1956, the quoted (E. & M. J. Metal and Mineral Markets) price range for electronic-grade quartz crystals was \$4.50 to \$50. per pound, according to size and grade. Most of the material consumed by oscillator manufacturers in California was being sold in the range of \$6 to \$10 per pound.

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## QUARTZITE AND QUARTZ

BY WILLIAM B. CLARK AND DENTON W. CARLSON

Silica, in the forms of quartzite, vein quartz, quartz gravel derived from vein quartz, and pegmatite quartz, has been mined in several areas in California. These materials have been used variously in ceramics, cement, ferrosilicon, metallurgical fluxes, abrasives, filtering media, poultry grits, and for numerous applications in the chemical industry. Of these materials, quartzite is mined most abundantly in California. It is used in the manufacture of regular and super-duty silica bricks and as a source of silica in portland cement. Only small amounts of vein quartz, quartz gravel, and pegmatite quartz are being mined in the state.

*Mineralogy and Geologic Occurrence.* Quartz ( $\text{SiO}_2$ ), one of the most abundant minerals, comprises about 12 percent of the earth's crust. The mineral crystallizes in the hexagonal system and occurs as crystals and crystal aggregates as well as in massive and granular forms. Quartz ordinarily is colorless to white, but impurities may cause it to show a wide color range. It has a hardness of 7 (Mohs' scale) and a specific gravity of 2.65. Quartz has a vitreous or glassy luster and generally is transparent to translucent. Although soluble in hydrofluoric acid, it is insoluble in ordinary acids.

Thermal studies show that quartz is one of several crystalline forms of silica, each of which is stable in a particular temperature range. Quartz itself exists in two modifications, low quartz (alpha) and high quartz (beta), which differ slightly in most of their physical properties. Low quartz forms at temperatures below  $573^\circ \text{C}$ . At  $573^\circ \text{C}$ , low quartz undergoes a reversible and nearly instantaneous inversion to high quartz. About  $870^\circ \text{C}$ , it is unstable, and if time is allowed for equilibrium to be attained, it inverts to tridymite, which is stable from  $870^\circ \text{C}$ . to  $1470^\circ \text{C}$ . or cristobalite, which is stable from  $1470^\circ \text{C}$ . to  $1710^\circ \text{C}$ . Above  $1710^\circ \text{C}$ , silica is a liquid. Unlike the inversion of low quartz to high quartz, the inversions between quartz, tridymite, and cristobalite occur slowly and are not reversible. Quartz can persist at temperatures greater than  $870^\circ \text{C}$ . Tridymite and cristobalite, once formed, can exist indefinitely at room temperature (Sosman, 1927, pp. 41-85).

Quartz is a major constituent of acidic igneous rocks such as granite, granodiorite, rhyolite, dacite, and granite pegmatite. It is the most abundant vein mineral and commonly forms the gangue of ores. Because quartz is highly resistant to chemical weathering and rarely alters to other substances, sandstones composed of quartz grains have formed throughout geologic time. In many places these have been metamorphosed to hard, compact, quartz-rich rock known as quartzite. Quartz also is commonly present in gneiss, schist, slate, and shale.

Quartzite is a compact and tough rock and consists essentially of a mosaic of quartz grains held together by a siliceous cement. It is characterized by a splintery fracture that breaks across both the grains and cement. Most quartzite bodies are interbedded with other metasedimentary rocks, and range from minute layers to bodies several hundred or more feet in thickness and thousands of feet long. Common impurities include feldspar, mica, and iron minerals derived from the other constituents of the original sandstone, as well as small

interbeds of slate, limestone, and schist. Pure quartzite sometimes is known as "ganister".

Most quartz veins are genetically related to plutonic igneous rocks of acidic composition and have been deposited in fissures during the end stages of the consolidation of such rocks. Quartz veins are especially common in metamorphic rocks near granitic bodies. Quartz veins range from small stringers less than an inch wide to those many tens of feet wide and several thousand feet long. A typical quartz vein consists of an interlocking aggregate of anhedral to subhedral crystals. Some veins are barren of any other mineral, whereas others contain various amounts of sulfides (chiefly pyrite), native gold, calcite, ankerite, talc, and limonite. Quartz gravels consist of pebbles, cobbles, and boulders derived from quartz veins and occur in stream channels.

Quartz is a particularly conspicuous constituent of granite pegmatite bodies where it generally is associated with feldspar. In such bodies, quartz-feldspar mosaics commonly consist of grains several inches to a few feet in diameter. Some pegmatites contain lenticular to pod-like cores of quartz as much as several tens of feet in diameter.

To be of commercial interest, deposits of quartzite, vein quartz, or pegmatite quartz generally should contain at least 97 percent silica, be suited to inexpensive mining methods, and be near to transportation facilities.

*Localities in California.* Quartzite, vein quartz, and quartz gravel are widespread in California. Quartzite occurs in the desert regions, Klamath Mountains, Coast Ranges, Sierra Nevada, and Peninsular Ranges. Quartz veins are most abundant in the western Sierran foothills, but also are common in portions of the Peninsular Ranges, Transverse Ranges, Klamath Mountains, the desert regions of eastern and southern California, and in a few areas of the Coast Ranges. Quartz gravel is common in portions of Recent and Tertiary stream channels in the Sierra Nevada. Most of the granitic pegmatites are in the Peninsular Ranges in San Diego and Riverside Counties.

Quartzite known to be suitable for commercial silica occurs in the desert regions of southern and eastern California. Usable quartzite may be discovered in other parts of the state as the demand for silica increases. Most of the quartzite mined in California has been obtained from San Bernardino and Inyo Counties. The Oro Grande area of San Bernardino County has been the principal source of quartzite in California, and in recent years has yielded as much as several thousand tons of quartzite annually. In this area, massively bedded quartzite of the Oro Grande and Hodge series occurs in extensive bodies as much as 250 feet thick and several thousand feet long. The principal producers of quartzite from this area have been the Mineral Materials Company and the Riverside and Southwestern Portland Cement Companies. The output of the Mineral Materials Company's operation has been used in the manufacture of silica brick by the General Refractories Company at the Los Angeles plant and in cement manufacture at the nearby plant of the California Portland Cement Company. Part of the output of the Southwestern Portland



Cement Company has been sold to Gladding, McBean and Company for silica brick manufacture (Bowen, 1954, p. 178). Years ago the Atlas Fire Brick Company mined quartzite west of the town of Hodge, also in San Bernardino County, for use in silica brick. All of these have been open-pit operations.

Large tonnages of especially pure quartzite are contained in the Eureka quartzite, an Ordovician formation which is extensively exposed in Inyo County and through a large part of Nevada. In Inyo County this formation is generally 200 to 400 feet thick and forms gently to steeply dipping bodies hundreds to thousands of feet long. It is prominently exposed in the Inyo Mountains, both the northern and southern parts of the Panamint Range and the Funeral Mountains. However, most of these occurrences are of difficult accessibility and only at two localities, both low on the western slope of the Inyo Mountains and along the east margin of Owens Valley, has the Eureka quartzite been mined commercially. Quartzite operations in this area are favored by nearness to paved highways and to rail facilities. Sampling of the quartzite in this area has shown that it persistently contains 0.25 percent or less combined alumina and alkalis which are the principal impurities in quartzite to be used in the manufacture of refractory brick (Richard F. Brooks, Gladding, McBean and Company, personal communication, 1955).

The Eureka quartzite was first quarried in the Owens Valley area in 1955. The site of the original quarry is about 2½ miles northwest of Keeler, but in 1957 operations were moved to a point about 4½ miles farther northwest. The material has been crushed at the quarries and trucked to a nearby stock pile on the railroad. It has been used in the manufacture of silica brick, in the Los Angeles area, by Gladding, McBean and Company and by the General Refractories Company.

In the western foothills of the Sierra Nevada, massive quartz veins occur in metamorphic rocks of Jurassic and Paleozoic age and in granitic rocks. These veins are most abundant in the Mother Lode belt, which is about 120 miles long. The Mother Lode itself is a system of linked quartz veins that occupies a zone of reverse faulting (Knopf, 1929, p. VII). Many of the veins contain gold and sulfides and have been major sources of gold. In some places, however, the veins are nearly barren of other minerals and have been mined locally as sources of silica. Mother Lode veins range from a few to as much as 50 feet in width. All have steep dips. Massive quartz veins also are found east and west of the Mother Lode.

Deposits of quartz gravel consist of pebbles, cobbles, and boulders of vein quartz mixed with sand, clay, and pebbles, cobbles, and boulders of igneous and metamorphic rock. In the area of Bear River in Nevada and Placer Counties, and in Tertiary channels in the Dutch Flat area of Placer County, the percentage of quartz gravel has been sufficiently high as to provide a commercial source of silica.

The principal source of vein quartz in the western Sierra Nevada has been at White Rock in western Mariposa County west of the Mother Lode. Here a massive vein of white "bull" quartz 300 feet long and 150 feet wide was quarried by the Kaiser Aluminum and Chemical Company from 1942 to 1952. The quartz was used in the manufacture of ferrosilicon at Permanente, Santa

Clara County. During 1952-53, this concern utilized quartz gravel for the same purpose, and obtained it from the Bear River north of Colfax, Placer County. Since 1955, small amounts of quartz have been quarried from a massive Mother Lode vein north of Coulterville in Tuolumne County. The quartz is crushed and marketed as poultry grit.

Vein quartz in the Sierran foothills formerly was mined at the Harvard gold mine in Tuolumne County in 1926; at Carson Hill, Calaveras County in 1924; at White Rock Canyon north of Placerville, El Dorado County intermittently from 1916 to 1934; near Friant, Fresno County in 1936; and near Auburn, Placer County about 1922. Quartz gravel was mined in the Gorge, Alta, and Dutch Flat areas of Placer County, and near Placerville, El Dorado County, during the 1920's. The quartz from these operations was used as a fluxing material in steel furnaces, as an abrasive in scouring powders, and in stucco.

Vein quartz also has been mined in the Transverse Ranges in Los Angeles County. Here, massive quartz veins occur in metamorphic rocks of the Pelona schist series and the San Gabriel metamorphic complex. Since 1951, small amounts have been quarried 7 miles north of Glendora and used in ceramics, insulating material, and various types of filters. Vein quartz was mined in the Sierra Pelona, Mint Canyon, and Antelope Valley areas chiefly prior to 1925. These were short-lived operations that supplied raw materials for glass manufacturing. Minor amounts were obtained from a quartz vein in the Coast Ranges west of Patterson, Stanislaus County, in 1943. Years ago gold-bearing quartz was mined in the Klamath Mountains northwest of Redding for use as siliceous flux in copper smelting.

Pegmatite quartz has been obtained chiefly in the Peninsular Ranges of San Diego and Riverside Counties and to a lesser extent in Kern and Imperial Counties. The quartz has been produced intermittently, largely as a by-product of feldspar mining (see section on feldspar in this volume). Most of these operations are idle. The quartz was used in abrasives and ceramics.

The largest operations in the Peninsular Ranges were those of the American Encaustic Tiling Company which mined feldspar and quartz in an extensive pegmatite zone near Murrieta, Riverside County, during the 1920's and early 1930's. This concern also mined deposits near Nuevo and Winchester, also in Riverside County, and west of Jacumba, San Diego County. The Flynt Silica and Spar Company mined feldspar and quartz from pegmatites north of Live Oak Spring, San Diego County, during the 1920's; during the 1930's these properties were operated intermittently by other concerns. From time to time, small amounts of quartz are mined from a pegmatite in granite northwest of Rosamond, Kern County. It is crushed and used in concrete slabs for building facing. Other pegmatite deposits, from which by-product quartz has been obtained, are south of Hemet, south of Lakeview, north of Winchester, and near Perris, all in Riverside County, and in the Jacumba, Descanso, Warner Hot Springs, and Campo areas of San Diego County.

*Mining and Treatment.* Quartzite, vein quartz and quartz gravel are mined mostly by open-pit or quarrying



methods; pegmatite quartz has been obtained partly by underground mining. In the grinding and preparation of these materials for market, several methods are used. The choice of methods depends upon the type of raw material and the character of the product desired. Crushing is done in jaw crushers. For fine grinding, pebble, tube, or ball mills or dry pans are used. Sizing is done by screening or by some system of water classification or air separation. As massive quartz and quartzite are hard and tough, crushing and grinding are expensive. In order to lower costs, at some plants the rock is calcined before crushing. Because of an increase in the demand for very fine sizes and the difficulty in producing them by conventional grinding processes, silica in the 0.01-0.05 micron range is usually produced by chemical means. One such process involves burning ethyl silicate, a volatile liquid, and collecting the vapor which consists of pure silica. In the manufacture of silica brick, quartzite is crushed and ground. Quartzite used in portland cement is crushed, proportioned with limestone and other materials, and then ground to proper size for kiln feed. For ferrosilicon, vein quartz or quartz gravel is crushed to a 1- to 3-inch size.

*Utilization.* Quartzite is used in the manufacture of silica bricks and as a silica source in portland cement. It also is used as crushed and broken stone, as an abrasive, and as dimension stone (see respective sections on these commodities in this volume).

In the manufacture of silica brick, the ground quartzite is mixed with 1 to 3 percent by weight of hydrated high-calcium lime. The material is then pressed into brick shapes and fired in either periodic or tunnel kilns. During firing, the composition of the brick changes from quartz to 50 to 60 percent tridymite, and 30 to 40 percent cristobalite with some residual quartz and siliceous glasses, and the brick undergoes a permanent expansion of about 3.5 percent (Brooks, 1955).

In California, silica bricks are used chiefly in open-hearth steel furnaces. Silica brick is an acid refractory material of comparatively great strength at high temperatures. Because of its acid chemical reaction it is used to line furnaces that contain siliceous melts. Its high temperature strength makes it suitable for parts of basic furnaces such as walls and roofs that are not in contact with basic melts. Other uses for silica brick include acid open-hearths, coke ovens, gas retorts, vertical lime kilns, tunnel kilns, electric steel furnaces and reverberatory furnaces.

Two types of silica brick are manufactured in the state, regular- and super-duty. Regular-duty silica brick has been manufactured for many years. Super-duty silica brick, which was developed during World War II, has a higher deformation temperature than the standard grade. They are particularly useful in the roofs of open-hearths because they permit higher operating temperatures than can be attained with regular-duty silica brick.

Quartzite is most suitable for silica brick because of the physical nature of the grains and cementing material; vein quartz is unsuitable. When finely ground, quartzite forms fragments of irregular size and shape that overlap and interlock. This gives the brick great strength. For use in regular-duty silica brick, quartzite should contain no more than 1 percent alumina and alkali and for super-duty brick, no more than 0.5 per-

cent of these impurities. Quartzite of high purity is desirable for portland cement and should be uniform so proper kiln feed can be controlled.

Vein quartz, quartz gravel, and pegmatite quartz have been used in the manufacture of ferrosilicon and, to a lesser extent, in metallurgical fluxes, poultry grits, glass, stucco, insulating material, filters, abrasives, and ceramics. In the production of ferrosilicon, the crushed vein quartz or quartz gravel is heated with iron ore or scrap iron and a reducing agent of charcoal or coke in electric furnaces. Ferrosilicon is used in the manufacture of magnesium by the silicothermic method and in the steel industry as a cleansing or deoxidizing agent as well as to give steel certain desired physical characteristics (see sections on iron and magnesium in this volume). For ferrosilicon, quartz of high purity (97 percent or more  $\text{SiO}_2$ ) is desirable, although the presence of iron oxide is not objectionable. However, the presence of arsenic or phosphorus is very objectionable as poisonous gases are formed. In smelting, silica is needed for slagging purposes. The presence of recoverable metals such as gold and silver is desirable, but lime and magnesia are detrimental. Pulverized silica, prepared from crushed quartz or silica sand, is used in ceramics as an ingredient of whiteware bodies and glazes, as an abrasive, and as a mineral filler or extender. Silica for many of these purposes must have high purity, and often a high degree of whiteness is specified. Much of the pulverized silica used in California is made from quartz from out-of-state sources, especially Arizona.

*Markets.* Currently the chief marketing area for quartzite in California is the southern part of the state. In addition to the silica brick manufactured by Gladding, McBean and Company at South Gate and the General Refractories Company at Los Angeles, it is also manufactured by the Harbison-Walker Refractories Company at Warm Springs, Alameda County, but the quartzite used at this plant is brought from Oregon. The quartzite-consuming cement companies in southern California now own or lease their own deposits and hence have their own sources of supply. However, the demand for silica brick and cement is increasing, and several concerns are conducting exploration programs for new sources of raw material. Although most of these concerns wish to buy or lease undeveloped deposits, some possibly would purchase quarried and crushed material from an individual operator. Before embarking upon an extensive mining program, the owner of a deposit should have an assured market, and costs should be carefully calculated, as quartzite is worth but a few dollars per ton at the quarry.

A limited market exists for vein quartz, quartz gravel, and pegmatite quartz in California. No ferrosilicon is manufactured in this state; all of it is imported from the eastern United States. Minor amounts of crushed quartz are used in building materials or are purchased by poultry raisers for grits. The owner of a quartz deposit of possible economic value can attempt to sell his product to the already limited market or try to find new uses and develop new markets for these materials.

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# RARE EARTH ELEMENTS

BY LLOYD C. PRAY\*

Although the rare earth elements are little known metals, they constitute about one-sixth of the known elements. Some of the rare earth elements are more abundant in the earth's crust than many of the more familiar metals such as lead, tin, and molybdenum. The rare earths are somewhat similar in their chemical properties, and the minerals from which they are obtained commercially ordinarily contain most of them. Most industrial applications of the rare earths have utilized such mixtures in the ratio in which they are recovered from the minerals. The rare earths are becoming increasingly significant in modern industrial technology as new uses for these elements are developed, and the demand probably will increase both for the mixtures and for purified rare earth elements. At present the rare earths are used in industry principally in the production of special types of glass; in cores of carbon-arc electrodes for photographic and projection equipment; in pyrophoric alloy such as lighter "flints"; and as an additive to alloys of steels and lighter metals.

The largest deposit of high-grade rare earth minerals known in the western hemisphere—and with but one possible exception, in the world—occurs in the Mountain Pass district of southeastern San Bernardino County, California, where rare earths were discovered in 1949-50. Bastnaesite, a fluocarbonate mineral of the cerium group rare earths, forms about 10 percent of a body which has an areal extent of about 20 acres, and a minimum proven thickness of 50 feet. This deposit has sufficient easily mineable reserves to permit a many-fold increase in world consumption of the cerium group, the most widely used rare earths at the present time.

Most of the rare earths of commerce have been obtained from monazite, a rare earth phosphate, which is also the major source of thorium (see section on thorium in this volume). Large reserves of monazite occur in India and Brazil, where the mineral is recovered from "black sand" concentrates of beach or alluvial deposits. A monazite lode deposit of South Africa has been of major significance in recent years. The domestic reserves of placer monazite largely in Idaho and the southeastern Atlantic states, are now known to be appreciable. California contains both primary and placer deposits of monazite, but there has been little or no commercial production from these to date.

## GEOCHEMISTRY

The major rare earth elements, as they are usually classified, are 16 in number (table 1). All of the elements with atomic numbers from 57 to 71 are in the rare earth group. In addition, the element yttrium (atomic number 39) is also generally included, owing to its chemical similarity to the true rare earth elements. Some authorities include the elements scandium (Sc, atomic number 21), and thorium (Th, atomic number 90) in the rare earth group on the basis of certain similarities. Thorium is discussed elsewhere in this volume. Scandium is not closely related in mineral occurrence to the rare earths, and therefore is not considered in this article.

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Table I.

Element	Symbol	Atomic no.
Yttrium	Y	39
Lanthanum	La	57
Cerium	Ce	58
Praeseodymium } Didymium	Pr	59
Neodymium }	Nd	60
Promethium	Pm	61
Samarium	Sm	62
Europium	Eu	63
Gadolinium	Gd	64
Terbium	Tb	65
Dysprosium	Dy	66
Holmium	Ho	67
Erbium	Er	68
Thulium	Tm	69
Ytterbium	Yb	70
Lutetium	Lu	71

Most naturally occurring rare earth-bearing minerals contain mixtures of several rare earth elements of very similar chemical properties. The general similarity of chemical behavior of rare earth elements is explained on the basis of their atomic configuration. In general, if elements are arranged in order of increasing atomic number, each successive element differs appreciably in its chemical behavior from the preceding one, owing largely to the addition of one electron in the outer orbital electron shell of the atom. However, the rare earth group of elements from lanthanum to lutetium all have the same number of electrons in the outer orbital shell. The differences in electronic configuration of this unusual group are those of the number and distribution of electrons in one of the inner electron shells. A difference of the number of electrons in this inner level has much less effect on the chemical behavior of the element than if it were in the outer level, thus accounting for the similarity in behavior of the rare earth group.

Despite the similarities in chemical and physical properties, subtle differences do exist among the rare earth elements. These can be related largely to their different atomic weights, and to their slightly differing ionic sizes. The rare earth elements commonly are subdivided into two major groups, the cerium group which includes the elements from lanthanum to samarium (atomic numbers 57 to 62) and the yttrium group, which includes yttrium and the rare earths from gadolinium to lutetium (atomic numbers 64 to 71). Europium (atomic number 63) is placed in a separate category by some authorities, whereas others consider it to be a member of either the cerium or yttrium group.

The term "rare earth" was applied to the oxides of the rare earth metals prior to the discovery that these were similar but different metallic elements. The term is now applied collectively to all the metallic elements of the group. As initially applied, the term "rare earth" referred to rare earth elements in the oxide form. It is now used for any of the rare earth elements, regardless of whether they are in the metallic state, are combined with other elements to form oxides ("earths"), or are in other chemical compounds. Although the term "rare" appeared justified for nearly the first century after the discovery of rare earths, some of the rare earth elements, such as cerium, lanthanum, and neodymium, are present



in the earth's crust in the same order of abundance as the more familiar metallic elements of copper, cobalt, lead, nickel, and tin. With the exception of promethium, a short-lived radioactive rare earth element, all of the rare earth group are more abundant than bismuth, cadmium, and silver, and far more abundant than gold or platinum (Rankama and Sahama, 1950). The term "rare" is justified, however, as these elements are rarely concentrated into mineral deposits that contain as much as 1 percent of rare earths, whereas deposits of lead and copper commonly consist of high-grade masses.

### MINERALOGY

The rare earth elements occur in three major ways in the earth's crust. Much of the total rare earth content of the crust occurs in quantities ranging from a trace to a few percent in common rock-forming minerals, such as feldspar and amphiboles. Much of the remainder occurs as a major constituent of such minerals as monazite, allanite, or xenotime. These minerals, however, commonly are uniformly disseminated in the host rock, such as a granite, and form but a minor fraction of the rock mass. Some of the rare earth elements recently have been shown (Brown and Silver, 1955) to occur loosely bonded to mineral surfaces in igneous rocks. Most of commercial sources of the rare earths are beach or fluvial placer deposits. Primary concentrations of rare earth minerals are uncommon, but these include the bastnaesite deposit at Mountain Pass, California. Only a few of the known primary deposits of monazite are of sufficient size and grade to be mined largely for the rare earth and thorium content.

The major rare earth minerals of commercial importance are monazite and bastnaesite. Only bastnaesite has been mined commercially in California. In both monazite and bastnaesite nearly all of the rare earth elements are of the cerium group. The proportions of the elements in the bastnaesite ore from Mountain Pass, California, are about 50 percent cerium, 30 percent lanthanum, 14 percent neodymium, 4 percent praseodymium, and 1 percent samarium. At present, the main source of the yttrium group rare earths is the residue obtained in the processing of monazite for the cerium group rare earths. Xenotime, the phosphate of yttrium group rare earths, affords a source for some of the relatively small amount of yttrium group rare earths that is used industrially.

The major characteristics of these three minerals are indicated below; owing to the difficulty of recognition, however, optical and chemical tests should be used to confirm megascopic identifications of these minerals.

*Bastnaesite*, (RE)FCO<sub>3</sub>, is a fluo-carbonate of the rare earths of the cerium group. It has a hardness of 4.5, and a specific gravity of about 5. It ranges in color from light tan or honey colored to reddish brown and has a distinct resinous luster. Crystals are commonly of tabular or prismatic habit and belong to the hexagonal system.

*Monazite*, is a phosphate of rare earths of the cerium group. It may contain minor amounts of rare earths of the yttrium group. Thorium commonly forms 3 to 10 percent of the mineral. Monazite is generally honey-yellow to reddish brown in color, has a somewhat resinous luster, a hardness of 5 to 5.5 and a specific gravity

from 4.9 to 5.3. It is monoclinic, has perfect basal cleavage, good cleavage parallel to (100) and one or more inferior cleavages or partings.

*Xenotime* is the phosphate of rare earths of the yttrium group. It occurs in short, tetragonal prisms resembling zircon, and has perfect prismatic cleavage. Similar to bastnaesite and monazite, the colors range from pale cream and tan to reddish brown. The hardness is 4 to 5 and specific gravity ranges from 4.45 to 4.56.

A potential source of rare earths is pyrochlore, a rare earth columbate and tantalate mineral, now known to occur in several large, low-grade deposits in the world. Exploitation of this source is dependent upon the development of economic processes for beneficiation of the ore and for separation of the various metallic elements in pyrochlore. Many other minerals contain appreciable amounts of rare earths, but none forms an important commercial source of these elements at the present time. Included among the more common or potential commercial sources of rare earths are euxenite,\* fergusonite, and samarskite (all complex uranium-thorium-columbium-tantalum minerals) and two, allanite and cerite, which are iron-calcium-aluminum silicates of the rare earths. Although the leaching of certain igneous rocks by dilute acid (Brown and Silver, 1955) will remove rare earths, uranium, and other elements, this process is not commercially feasible now. It would, however, furnish a source of rare earths as by-products or co-products of uranium.

Prospecting for rare earth minerals is commonly aided by use of a radioactivity counter. This is particularly useful in detection of monazite deposits as the thorium is radioactive. Although bastnaesite is not radioactive, the Mountain Pass deposit was discovered with the aid of a geiger counter which responded to a low but detectable amount of thorium in the bastnaesite-bearing veins. Xenotime is normally radioactive. Alluvial concentrations of black sands should be checked for their mineral content by expert mineralogists so as to not overlook possible new sources of rare earth minerals as well as zircon, rutile, and other associated heavy minerals.

### RARE EARTH DEPOSITS OF CALIFORNIA

The only commercially significant rare earth deposit known in California at the present time (1957) is in the Mountain Pass district of northeastern San Bernardino County. This deposit is of an unusual mineralogic type, and is the largest single deposit of rare earths known in the western hemisphere. "Black sands" that contain small percentages of monazite are found in minor concentrations in various parts of California. In addition, rare earth-bearing minerals have been reported from numerous other localities in the state where they occur as minor constituents of primary deposits, but at which the rare earths are not known to occur in sufficient quantities to permit their economic recovery.

*Mountain Pass Area.* The Mountain Pass area of rare earth mineralization lies along and slightly east of the divide of the Mescal Range in northeastern San Bernardino County, California, on U. S. Highway 91, about

\* In 1957, some placer sands in Idaho were being processed for their content of yttrium earths, largely in the minerals euxenite and xenotime.



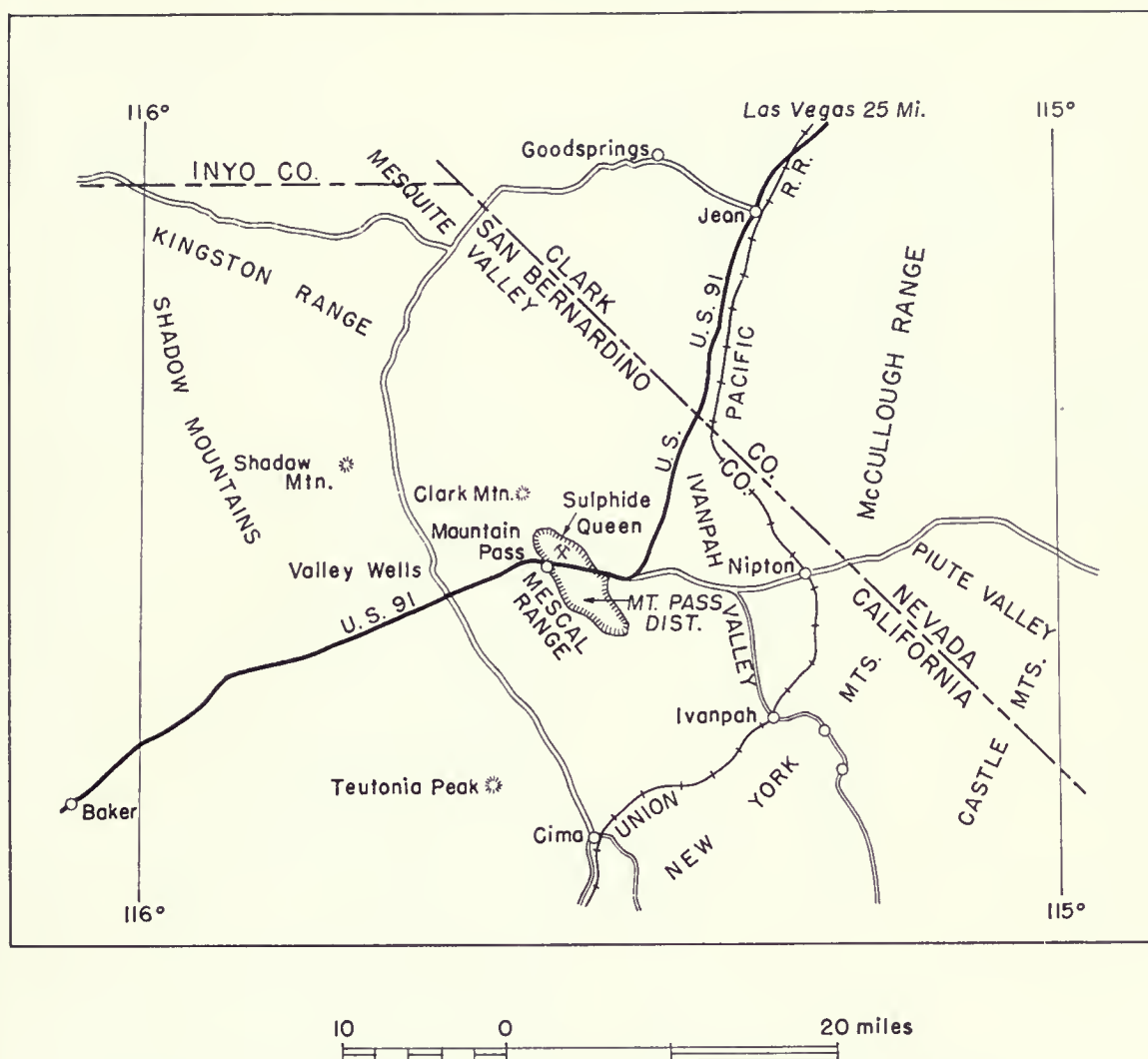


FIGURE 1. Index map of a part of eastern California, showing location of Mountain Pass rare earth district and Sulphide Queen mine.

60 miles southwest of Las Vegas, Nevada. The area is about seven miles long and three miles wide, and trends northwest. The rare earth deposit of the greatest commercial significance occurs about one-half mile northeast of the small settlement of Mountain Pass which is at a drainage divide on U. S. Highway 91. The area is a rolling upland of moderate relief, at an average elevation of 5,000 feet, and nearly all of the mineral deposits are easily accessible by road. About one-half of the district is covered by a thin veneer of alluvial debris.

Rare earth minerals were discovered in the district in April, 1949, by Herbert E. Woodward and Clarence Watkins. The presence of rare earths and the identity of bastnaesite as the major rare earth mineral was established independently by laboratory tests by E. T. Schenk of the U. S. Bureau of Mines and by D. F. Hewett of the U. S. Geological Survey. Subsequent prospecting by individuals and geologic investigations by members of the U. S. Geological Survey resulted in the independent discovery of the bastnaesite-bearing Sulphide Queen carbonate body in 1950, as well as numerous other minor vein deposits of rare earths within the district.

Initial attention was focussed on the high-grade bastnaesite veins at the discovery site area known as the Birthday claims (Pray and Sharp, 1951; Sharp and Pray, 1952), but with the discovery of bastnaesite in the large Sulphide Queen carbonate body in 1950, the center of interest shifted to the latter deposit. Since 1951, all of the rare earth production has been from the Sulphide Queen ore body. This single deposit contains rare earth reserves estimated at many times the combined reserves of all other deposits in the district. The Molybdenum Corporation of America owns nearly all of the claims in the Mountain Pass district, including the Sulphide Queen deposit and the Birthday claims.

A U. S. Geological Survey Professional Paper (Olson, Shawe, Pray, and Sharp, 1954) contains the most comprehensive geologic data yet published and includes a complete history, by Hewett, of the discovery. A summary of the geological relationships in the Mountain Pass district is given by Olson and Pray (1954), and data pertaining to the surrounding area have been recently published by Hewett (1956).



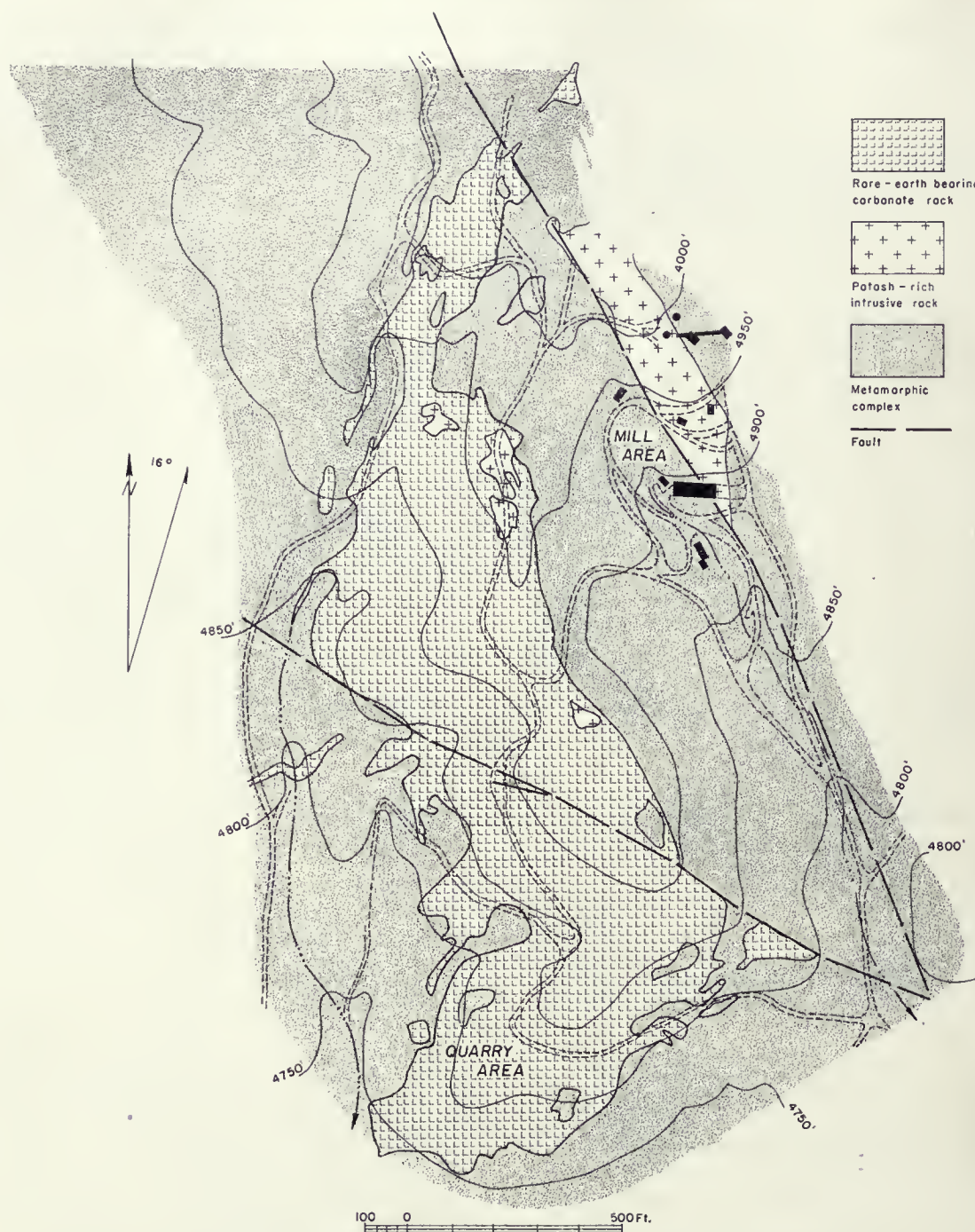


FIGURE 2. Generalized geologic map of Sulphide Queen rare earth deposit, San Bernardino County.

The Mountain Pass rare earth deposits lie in a belt of pre-Cambrian metamorphic and igneous rocks which is exposed in an elongate northwest-trending fault block. A northwest-trending fault directly north of the Birthday shaft and less than one-half mile north of the Sulphide Queen ore body appears to form the northern boundary of the area of rare earth mineralization. Two transverse faults each with left lateral movement and of northwesterly trend, appear to offset the southern part of the mineralized zone.

The pre-Cambrian metamorphic and igneous complex consists largely of (1) hornblende and mica gneisses and schists, (2) granitic augen gneisses and minor associated pegmatites, and (3) minor intrusive igneous rocks many of which are of potash-rich, quartz-poor types such as shonkinite and syenite. This complex is intruded by Tertiary (?) dikes predominantly of andesitic composition, but including rhyolites and basalts.

The potash-rich rocks comprise seven large intrusive bodies and several hundred thin dikes. The largest of these intrusive bodies consists of shonkinite and mafic



syenite, is about 6,000 feet long and 1,800 feet wide, and occurs in the Sulphide Queen and Birthday claims area. The other six intrusive masses lie south of U. S. Highway 91. Of these, three are composite shonkinite-syenite bodies, two are leucosyenites, and one is granitic. In general, the oldest of these intrusive rocks are the coarse-grained shonkinites which are composed of about equal proportions of biotite, green augite, and purplish-pink microcline feldspar. The successively younger rocks of this intrusive sequence are finer grained, and contain more feldspar and quartz and a lower percentage of mafic constituents. Of the latter, amphibolites occur in place of the augite in the younger intrusives, and also contain augite and biotite. They are more feldspathic, however, and contain quartz. Local dikes of fine-grained shonkinite are exceptions to this rule, and appear to be the latest of the potash-rich rocks. Determinations based on studies of the zircon in the shonkinite indicate a late pre-Cambrian age (Jaffe, 1955).

The rare earth minerals, principally bastnaesite, occur in numerous thin veins and in the one large body known as the Sulphide Queen ore body. All of these deposits consist largely of calcite and barite. The veins are somewhat younger than the potash-rich intrusive rocks. Indeed, the intrusion of the differentiated series of the potash-rich igneous rocks and the rare earth mineralization appear to have been parts of a single cycle that ended with injection and hydrothermal replacement of both the igneous rocks and their metamorphic hosts by carbonate-rich, rare earth-bearing materials. A pre-Cambrian age for the Sulphide Queen carbonate body has been determined by studies of the radioactivity of its contained monazite (Jaffe, 1955).

The Sulphide Queen ore body contains by far the largest known reserves of rare earth minerals in the Mountain Pass area. It outcrops over an area of about 20 acres and covers most of the western side of a north-trending ridge. The body is nearly half a mile long and 500 to 700 feet in width along its southern half. It tapers irregularly toward the north, and dips moderately westward. It is known to extend to depths of 50 feet under most of the surface outcrops, and geologic evidence suggests it persists to much greater depths. The body consists largely of calcite, 20-25 percent barite and 5 to 15 percent bastnaesite. One vein-like mass within the body contained as much as 50 percent bastnaesite over a width of several tens of feet, but most of the bastnaesite is rather uniformly disseminated throughout the body. Quartz is a ubiquitous minor mineral. Other carbonate minerals include dolomite and ankerite. Some of the barite contains appreciable strontium, locally forming the mineral barian celestite. Other rare earth minerals present, but not of commercial importance, include parisite, monazite, allanite, samamallite, and cerite.

The Sulphide Queen carbonate body is crudely foliated. It contains local inclusions of potash-rich igneous rocks and metamorphic rocks. The geologic evidence suggests that the body was intruded as carbonatite. Subsequent to emplacement, the mass has been somewhat faulted and locally altered and recrystallized.

Precise data on rare earth reserves of the district are not available. Nearly all of the reserves are in the Sulphide Queen ore body. Drilling of the body to a depth of 50 feet has proved the existence of a block 50



FIGURE 3. View of main quarry, Sulphide Queen rare earth deposit, San Bernardino County.

by 400 by 1,000 feet that contains more than 10 percent rare earths (Anonymous, 1952). This would constitute more than 200,000 tons of rare earths, a figure many times greater than total world consumption of rare earth elements to date. As much of the body apparently persists to depths considerably greater than 50 feet, a total inferred reserve of the order of one million tons of rare earths seems to be a conservative estimate. The Sulphide Queen carbonate body, therefore, may well be the largest known concentration of rare earths in the world.

Most of the smaller concentrations of carbonate rock in the district form distinct veins, commonly a few inches to a few feet in width and as much as several hundred feet in length. Like the Sulphide Queen carbonate body, the veins consist largely of calcite, barite, and bastnaesite. In the Birthday claims area of the original discovery (Sharp and Pray, 1952), veins, a few feet thick, were found to contain bastnaesite crystals which were as much as 4 inches across and formed a third or more of the vein. These veins were mined for a short time prior to the discovery of the Sulphide Queen ore body, but their erratic nature in depth and narrow width make them much more costly to mine than the massive Sulphide Queen deposit. The mining of other rare earth-bearing veins of the district has been deterred for similar reasons.



FIGURE 4. View of rare earth mill of Molybdenum Corporation of America, Mountain Pass district, San Bernardino County.



The only rare earth ore currently (1957) mined in the Mountain Pass district is obtained from open pit quarry operations at several faces into the southwest and west central parts of the Sulphide Queen ore body. To date operations have not extended to levels below the level of the lowest outcrops of the body. The faces are blasted, ore loaded into trucks by power shovels, and thence trucked about a quarter mile to the mill site. Figure 3 shows the open cuts as they appeared in July, 1956.

The Sulphide Queen ore, as mined, has averaged 7 to 10 percent rare earth oxides, almost entirely derived from the mineral bastnaesite. The milling process has now been perfected to obtain a concentrate of 90 percent or more rare earth oxides, and only a low proportion of rare earths is lost in the tailings. The capacity of the present mill is approximately 150 tons per day. If the rare earth market were to improve appreciably, the capacity of the mining and milling operations could be increased manifold. Details of the mill circuit are given by Dayton (1956). The major steps in the process are outlined below:

Major process	Equipment type	Remarks
Crushers ----	Primary jaw crusher	Ore averages 7-10 percent rare earth oxide.
	Symonds cone crusher	— $\frac{3}{4}$ " mesh
	Rod mill	—10 mesh
Grinders ----	Marcy ball mill	
Classifier ----	Dorr classifier	Closed circuit with ball mill. Discharges—100 mesh.
Flotation ----	Fagergren and Agitair rougher cells	Heat pulp, reagents float bastnaesite and depress barite, calcite and quartz.
	Denver, 18-S cleaner cells, five stages	Rougher cells produce 35 percent rare earth concentrate and cleaner cells produce 63 percent concentrate.
Leaching ----	10 percent HCl	Dissolves calcite gangue.
Filtration ----	Eimco disc filter	Yields 72 percent rare earth oxide concentrate.
Calcining ----	Edwards roaster	Burns off fluorocarbonate content, yields 90 percent plus concentrate of rare earth oxides.

*Other Rare Earth Occurrences in California.* Although rare earths, mostly in the mineral monazite, are known from widely scattered localities throughout the state, the only deposits currently exploited, or, indeed, known to afford much promise, are those of the Mountain Pass district. Recent prospecting with geiger and scintillation counters has revealed many deposits containing monazite, especially in San Bernardino and Riverside Counties. Monazite occurrences in the state have been reviewed in detail by Walker, Lovering, and Stephens (1956) and are discussed in the section on thorium in this volume. The principal primary deposits that have been discovered to date are in the Rock Corral area of San Bernardino County, and the nearby Live Oak tank and Desert View areas of Riverside County, both near Twenty-nine Palms. In these deposits small amounts of allanite, monazite, and, locally, xenotime occur in biotite-rich lenses of gneissic rocks. The same

minerals also are disseminated in large bodies of quartz monzonite and related silicic plutonic rocks.

Monazite and xenotime have been reported to occur in pegmatites in the Southern Pacific silica quarry near Nuevo, in Riverside County. Monazite is also known in other pegmatites near Riverside; and in the pegmatites of the Pala and Mesa Grande areas, San Diego County (Chesterman, 1950).

Monazite occurs as a minor constituent of black sands throughout the state, especially in Butte County and the "Indian Diggins" district, and at Placerville, El Dorado County; Michigan Bluff, Placer County; the Brownsville district, Yuba County; Crescent City, Del Norte County; Trinidad, Humboldt County; and Redondo Beach, Los Angeles County.

Xenotime is probably as widely distributed, though less abundant than monazite. It has been reported in the Twenty-nine Palms area and near Nuevo, Riverside County (Walker, Lovering, and Stephens, 1956) and as a detrital mineral in Pacific beach sands (Hutton, 1952). No commercial occurrences are known in California.

#### UTILIZATION

Rare earths currently have many industrial uses, but no single use is predominant. With increasing availability of the individual elements of the rare earth group, many additional uses certainly will be found and the demand for rare earths, both as mixtures and as purified single elements, will increase. Most of the rare earths of commerce are those of the cerium group. As previously stated, for many uses, the constituent rare earth elements of the ore are not separated, but are used in roughly the proportions in which they occur in the two major source minerals—monazite and bastnaesite. Kremers (1949) reported that rare earth utilization was divided as follows: glass industry, 30 percent; carbon-arc electrode cores, 25 percent; misch metal and ferrocerium, 20 percent; and miscellaneous, 25 percent.

The fluorides and oxides of the cerium group rare earths are added to the carbon-arc electrode cores to cause more of the light to be emitted in the visible spectrum. The intense white light needed for the photography and projection of motion pictures, in high speed photography, and in searchlights is generally obtained by the use of these rare earth elements.

Rare earths are utilized in the glass industry for many special purposes. They are used as both coloring and decolorizing agents. Cerium oxide is used as an opacifier for porcelain sign coatings. The addition of 2 to 4 percent cerium oxide to glass permits absorption of ultraviolet light waves. Lanthanum oxide is used to make a non-corroding optical glass of high refractive index for lenses. High-purity cerium oxide is used for windows of nuclear reactors.

Many of the rare earth elements have been marketed as misch metal. In this substance the proportions of the rare earth elements are not fixed, but are essentially the same as the proportions in the monazite or bastnaesite ores from which the rare earths are extracted. The rare earths in misch metal are largely, or entirely, those of the cerium group. The mixture commonly is referred to as "cerium" in the trade. Russell (1954) indicates the approximate proportions of the rare earth elements in misch metal to be as follows: cerium, 50-55 percent;



lanthanum, 22-25 percent; neodymium, 15-17 percent; and other rare earths, 8-10 percent. Other published figures on the proportions of rare earth elements in misch metal vary somewhat from the above figures.

Misch metal is diluted with 15-40 percent iron to make ferrocerium or "sparking metal" which is used as "flints" for cigarette lighters, miners' lamps, and similar devices. Misch metal is alloyed with aluminum, copper, magnesium, zinc, and zirconium for specialized uses. Although most of the metallurgical uses of rare earths employ misch metal, rare earth oxides, derived from California bastnaesite, have been recently used in place of misch metal in some applications.

Rare earths added to aluminum and magnesium are reported to improve the alloy strengths of these metals at intermediate to high temperatures, and are, therefore, of importance in certain parts for jet engines, gas turbines, and similar equipment (Loring, 1951; Leontis, 1952). Rare earths also are reported to improve the forging and casting qualities of aluminum and magnesium alloys (Loring, 1951; McDonald, 1952a, 1952b).

Rare earth metals are used as deoxidizing agents in iron and can be used in copper and copper alloys. They are known to improve the electrical properties of silicon electrical steels. Minor amounts of rare earths are used as abrasives for polishing optical surfaces; as oxidizing agents in photography; in the tanning of leather; in compounding printing inks and phosphors; and many miscellaneous uses (Lamb, 1955).

A large potential market exists for rare earths in the manufacture of steel and steel alloys. The addition of about 1 to 2 percent rare earths to steel is reported to improve working qualities and to create a finer and stronger grain than exists in ordinary steel (Post et al., 1951; Russell, 1954). The development of a mass market in the steel industry would vastly increase consumption of rare earths, and cause an increasing dependence on Mountain Pass deposits. To date, however, the use of rare earth additives in steel has been limited to special high alloy types (Lamb, 1950). Nevertheless, a wider usage of rare earths in such steels would form an important domestic market.

A potential use, but one difficult to evaluate currently, is in nuclear reactors. Samarium, gadolinium, europium, and dysprosium absorb slow neutrons and thus can be utilized to control the rate of the nuclear reaction. Europium appears especially valuable for this purpose.

#### MARKETING AND PRICES

Several factors make the market for rare earths an uncertain one. Monazite, as a thorium-bearing material, is subject to the control of the Atomic Energy Commission, so that data pertaining to imports and consumption of monazite are classified. Moreover, as new sources of rare earths have been discovered and brought into production, such as the Mountain Pass deposit of California and the Van Rhynsdorp monazite lode deposit of South Africa, the availability and price structure has fluctuated markedly.

In the years just preceding World War II, the yearly world production of monazite, then the only significant source of rare earths, was about 4,000 to 5,000 tons. One ton of monazite is equivalent to one-half to two-thirds

of a ton of rare earth oxide. Domestic imports during 1941 to 1943 averaged about 4,300 tons and dropped off sharply in 1944 and 1945, the last period for which figures are available. Kremers (1956) reports that domestic rare earth consumption in 1956 was equivalent to about 4,000 tons of monazite annually. This is equivalent to about 2,500 tons of rare earths. Monazite prices depend on the proportion of rare earths and thorium. In 1954, the price ranged between \$300 and \$400 per short ton (Lamb, 1955). In 1955, the increasing availability of monazite from the high grade hydrothermal lode deposit of the Anglo-American Corporation in Van Rhynsdorp district of the Cape Province, South Africa, caused prices to drop as low as \$260 per ton. This has forced some domestic operators of marginal monazite deposits to curtail or cease operations, and has curtailed the production at Mountain Pass, California.

There is no fixed price schedule for bastnaesite concentrates. In 1954, the Molybdenum Corporation of America reduced the price of its roasted bastnaesite concentrate (essentially rare earth oxide) from \$1.50 to \$1.00 per pound. The quoted price has remained at \$1.00 since that time. The actual contract price for purchases is not known to the writer. The mill at Mountain Pass has a present reported capacity of 5,000 tons of rare earth concentrates per year, a figure larger than the current domestic consumption. In 1956 the level of production at Mountain Pass was far below capacity.

In 1955, misch metal was quoted at \$3.50 per pound, and ferrocerium at \$8.00 per pound. The prices of purified rare earth elements are much higher than ferrocerium. Small lots (5 grams) of purified rare earth elements were first commercially available in 1955.

#### OUTLOOK

The utilization of rare earths probably will be increased as new applications are discovered. A continuation of current uses can be expected to require several thousand tons of rare earths per year. Rare earth production will continue to be closely related with that of thorium, as much of the rare earth output is obtained from monazite. The world outlook for thorium has recently been reviewed by Davidson (1956), Franklin and Eigo (1955), and Kremers (1956). The following comments are derived largely from these sources: Currently the world has an over-supply of rare earths. The present productive capacity at each of the two major primary deposits (Van Rhynsdorp lode deposit of South Africa with a capacity of 10,000 tons of 70 percent monazite per year, and Mountain Pass deposit which could yield 5,000 tons of rare earth concentrate per year) approximates the world consumption of rare earths. In addition, placer deposits, such as those in Australia, Brazil, Ceylon and India can contribute additional thousands of tons of rare earths annually in the form of monazite. Lode deposits of monazite of potential commercial significance recently have been reported in the Lake Athabaska district of Saskatchewan, Canada.

A factor difficult to evaluate currently is the demand for thorium for atomic reactors. Several authorities (Kremers, 1956; Dunworth, 1955) have reviewed possible needs for thorium in this developing field. The consensus is that, even with an extensive usage of a thorium



reactor, the annual amount would not greatly exceed present productive capacity of the world's monazite operations.

Pyrochlore may also become important as a source of rare earths and influence the market outlook. If beneficiation and separation problems can be solved, large low-grade deposits of pyrochlore could afford a source of columbium, tantalum, thorium, uranium, and rare earths.

The immediate outlook for the Mountain Pass district of California is uncertain in the face of competition of the South African lode deposit of monazite, and to a lesser degree by some of the placer monazite production. An increasing demand for thorium would provide an equally increasing problem to the producer of a rare earth mineral that contains little or no thorium. Much effort is being devoted currently toward development of new uses for rare earths. This effort should eventually lead to an appreciable increase in demand and to an extensive development of the Mountain Pass rare earth deposits. As a strategic domestic reserve of rare earths, the Mountain Pass area already is of prime importance.

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## SALINES

BY WILLIAM E. VER PLANCK

The salines are the natural soluble salts which occur in saline solutions and as soluble residues derived from the evaporation of solutions. Deposits of saline minerals are found only in arid regions unless they have been buried and protected from solution. Saline commodities of commerce include borates, bromine, calcium chloride, iodine, nitrates, potassium salts, sodium chloride or common salt, sodium carbonate, and sodium sulfate, all of which except nitrates are of commercial importance in California. Gypsum, because of its geologic occurrence and origin, is included, although it commonly is classified with the structural materials. Compounds of lithium, magnesium, and strontium may be conveniently included because in California they are now recovered mostly from saline sources. In 1953 the value of the salines produced in California amounted to \$41,511,000, or about 18 percent of the value of all mineral commodities exclusive of mineral fuels.

*Source of the Soluble Salts.* Dissolved minerals are to be found in almost all water. Many of the soluble salts are derived from the weathering of rock-forming minerals. Carbon dioxide of the atmosphere dissolves in water to form a weak solution of carbonic acid that slowly attacks silicates. Feldspars, for example, are broken down to insoluble clay minerals and carbonates of potassium, sodium, and calcium that are carried away in solution. Soluble sulfates result from the action of sulfuric acid derived from the weathering of sulfides, particularly pyrite. The weathering of silicates does not produce the quantities of chlorides and borates found in some waters. An important part of the sodium chloride of terrestrial waters is sea water that has been trapped in the interstices of marine sediments. Borates and perhaps part of the chlorides are thought to be derived from hot springs associated with volcanism or from the leaching of volcanic ejecta.

These soluble products find their way into rivers. The dissolved solids content of the California rivers ranges from 2,412 parts per million in the Santa Maria River at Santa Maria to 65 parts per million in the Merced River at Merced Falls. The California rivers vary also in the relative proportions of the dissolved solids. In most of them carbonate predominates, but some are high in sulfate. The chloride concentration is in all cases lower than the carbonate or sulfate concentration. In a similar way, the relative abundance of magnesium, calcium, and sodium varies from river to river. The proportion of magnesium is less than that of calcium or sodium, but the number of rivers high in sodium is about equal to the number high in calcium.

River water finds its way to the sea or to undrained basins where the dissolved solids accumulate. The salinity of the sea varies, but the following analysis of the dissolved solids may be taken as representative.

In a comparison of sea water with average river water, two facts are apparent. The first fact is that the relative abundance of the dissolved solids is reversed. In average river water calcium carbonate and calcium sulfate are the most abundant salts, while sodium chloride is of minor importance. In sea water, however, sodium chlor-

*Average dissolved solids content of  
river water throughout the world \*.*

<i>Percent of dissolved solids</i>	
CO <sub>3</sub> -----	35.15
SO <sub>4</sub> -----	12.14
Cl -----	5.68
NO <sub>3</sub> -----	0.90
Ca -----	20.39
Mg -----	3.41
Na -----	5.79
K -----	2.12
Fe <sub>2</sub> O <sub>3</sub> Al <sub>2</sub> O <sub>3</sub> -----	2.75
SiO <sub>2</sub> -----	11.67
<hr/> 100.00	

*Analysis of total dissolved solids in sea water †.*

<i>Percent of dissolved solids</i>	
Cl -----	55.292
Br -----	0.188
SO <sub>4</sub> -----	7.692
CO <sub>3</sub> -----	0.207
Na -----	30.593
K -----	1.106
Ca -----	1.197
Mg -----	3.725
<hr/> 100.000	

Dissolved solids content 3.301 percent to 3.737 percent.

\* Clarke, F. W., 1924, p. 119, analysis F.

† Clarke, F. W., 1924, p. 127, analysis A.

ide is far more abundant than the other salts. The second fact is that the chloride concentration in the sea is in excess of sodium, while in rivers the opposite is true. When river water reaches the sea, calcium carbonate is precipitated or withdrawn by organisms, and sulfates probably precipitate also. No simple explanation, however, is apparent for the excess of chloride over sodium in the sea.

*Classification of Brines.* Although no two saline waters are exactly alike, they may be classified into three main types based on the predominating acid radical. First is the chloride type which includes sea water as well as many terrestrial brines. Second is the sulfate type, and third is the alkali or volcanic type which is characterized by carbonate. Many alkali brines contain substantial amounts of sulfate and borate in addition to carbonate, but chloride is present in subordinate amounts. The three types grade into one another. The metallic ions in greatest abundance are sodium, potassium, calcium, and magnesium. Chloride and sulfate brines are found in regions of sedimentary rocks, and alkali brines occur where volcanic rocks are abundant. Ground water in granitic areas is likely to contain only 100 parts per million or less of dissolved solids, mostly calcium carbonate and silica.

*The Formation of Saline Minerals.* Almost all deposits of saline minerals have been formed by the evaporation of brines. In general, salts crystallize in inverse order of their solubilities, although temperature and the presence of other dissolved salts may modify the order of deposition. In 1849 Usiglio evaporated water from the Mediterranean Sea to determine the order of precipita-





FIGURE 1. Map of California showing location of saline deposits (borates, bromine, calcium chloride, gypsum, iodine, potassium salts, salt, sodium carbonate, sodium sulfate).



tion of sea salts. When the volume of the water had been reduced one-half, calcium carbonate, magnesium carbonate, and ferric oxide began to precipitate. At 20 percent of the original volume these materials were completely removed from solution, and gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) began to form. When the volume reached 15 percent of the original, most of the gypsum had precipitated; but some continued to come out down to 3 percent. Salt ( $\text{NaCl}$ ) began to form in quantity when the volume was reduced to 10 percent and continued to 1.6 percent. Magnesium sulfate and magnesium chloride precipitated in the same range, but the greater part of these salts formed after most of the sodium chloride had come out of solution.

From many terrestrial chloride brines the precipitation of sodium chloride follows that of the slightly soluble calcium carbonate and gypsum; but if much sulfate is present, sodium sulfate may crystallize before sodium chloride, especially in cold weather. Many alkali brines yield trona ( $\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$ ) rather than sodium chloride or sodium sulfate.

The mother liquor from which the salts of moderate solubility have precipitated is called *bittern*. Sea water bittern is rich in the chlorides and sulfates of magnesium and contains smaller amounts of potassium and bromine. The high magnesium content distinguishes it from bitterns derived from terrestrial chloride brines. Alkali brines yield bitterns containing alkali borates, carbonates, chlorides, and sulfates.

The desiccation of bittern yields highly soluble salts, many of which are complex. Bittern salts of marine origin include such minerals as:

Sylvite	-----	KCl
Carnalite	-----	$\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$
Kieserite	-----	$\text{MgSO}_4 \cdot \text{H}_2\text{O}$
Polyhalite	-----	$2\text{CaSO}_4 \cdot \text{MgSO}_4 \cdot \text{K}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$
Langbeinite	-----	$\text{K}_2\text{SO}_4 \cdot 2\text{MgSO}_4$
Boracite	-----	$5\text{MgO} \cdot \text{MgCl}_2 \cdot 7\text{B}_2\text{O}_3$

In contrast, the principal minerals associated with the alkali brine of Searles Lake, San Bernardino County, are:

Halite	-----	$\text{NaCl}$
Hanksite	-----	$9\text{Na}_2\text{SO}_4 \cdot 2\text{Na}_2\text{CO}_3 \cdot \text{KCl}$
Trona	-----	$\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$
Borax	-----	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$
Glaserite	-----	$3\text{K}_2\text{SO}_4 \cdot \text{Na}_2\text{SO}_4$

In nature usually only portions of the ideal, complete series of saline residues are found. Large deposits of pure gypsum and pure salt are well known, but deposits of bittern salts are rare and commonly consist of mixtures of several salts.

The undrained basins of the California deserts are ideal localities for the concentration by evaporation of dilute mineral-bearing water. Salton Sea is a saline lake that was formed in 1905-06 by a flood of fresh water from the Colorado River. If it were not replenished by drainage from the irrigation systems of the Imperial and Coachella Valleys, Salton Sea would have dried up between 1925 and 1930; but since about 1920 evaporation and inflow have been roughly equal. The salinity of Salton Sea more than doubled between 1916 and 1953, and today is it approximately that of sea water. Probably the additional dissolved solids came from the nearly fresh irrigation water that has been flowing into Salton Sea.

An undrained basin in a region of high evaporation is likely to have a playa of intermittent lake in its lowest part. Playas ordinarily are dry, but after heavy rains they may be covered by a few inches of water. One type of playa is free from salines and contains only fine-grained, impervious elastic sediments. In another type, brine exists within 10 feet of the surface; and the subsurface above the water table is moist. The elastic sediments contain disseminated crystals of salts, and the playa surface may have an efflorescent crust of salts formed by the evaporation of brine drawn up by capillary action. A third type of playa contains crystal bodies or beds of salts more or less free from elastic sediments. A crystal body may consist of a single salt or a mixture of several salts; often it is porous and contains a residual mother liquor that is in chemical equilibrium with the solid salts. Crystal bodies probably form by the precipitation of salts in saline lakes. Many of the basins in California that now contain playas held lakes in Quaternary time, but crystal bodies are believed to have formed only in those basins that received the clarified drainage of a large area for a long time.

Under favorable circumstances saline deposits may be covered with impervious mud that protects them from re-solution. The deposits in the Quaternary lakes are substantially as they were when they were formed, but saline deposits also occur in older rocks that have been folded and faulted.

Efflorescent deposits of saline minerals are not restricted to playas. Efflorescent crusts of calcium carbonate are called *caliche*. Black alkali and white alkali soils contain efflorescent deposits of sodium carbonate and sodium sulfate respectively. Much of the gypsum produced in California has come from the San Joaquin Valley where earthy deposits of gypsum and silt called *gypsite* form surface layers as much as 3 feet thick.

*Owens and Searles Lakes.* Searles Lake, which contains the largest known saline deposit in California, is a playa in which water stands above the surface only after heavy rains. Owens Lake, now a playa, was a saline lake until its inflow was decreased with the completion of the Los Angeles aqueduct in 1913. These are two of a series of dry lakes which during Pleistocene time had an integrated drainage. Owens Lake had an outlet to Searles Lake through Indian Wells Valley and Salt Wells Valley, alluvium-filled basins that are thought to have acted as settling basins and to have provided clear water to Searles Lake. Searles Lake in turn emptied into Panamint Valley and probably Death Valley.

Today Searles Lake is a vast flat of mud and sand containing disseminated salt crystals. Near its center is a permeable crystal body which averages 71 feet in thickness and has an exposed area of 12 square miles. The interstices, amounting to about 50 percent of the total volume, contain strong brine in chemical equilibrium with the soluble salts. Surrounding the exposed body is a 20-square-mile area where commercial salt bodies as much as 30 feet thick are covered by playa mud. A second crystal body 35 feet thick lies beneath the upper and is separated from it by 10 to 15 feet of impervious mud in which salts are disseminated.

The principal salts of the upper body are halite ( $\text{NaCl}$ ), hanksite ( $9\text{Na}_2\text{SO}_4 \cdot 2\text{Na}_2\text{CO}_3 \cdot \text{KCl}$ ), glaserite ( $3\text{K}_2\text{SO}_4 \cdot \text{Na}_2\text{SO}_4$ ), trona ( $\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$ ),



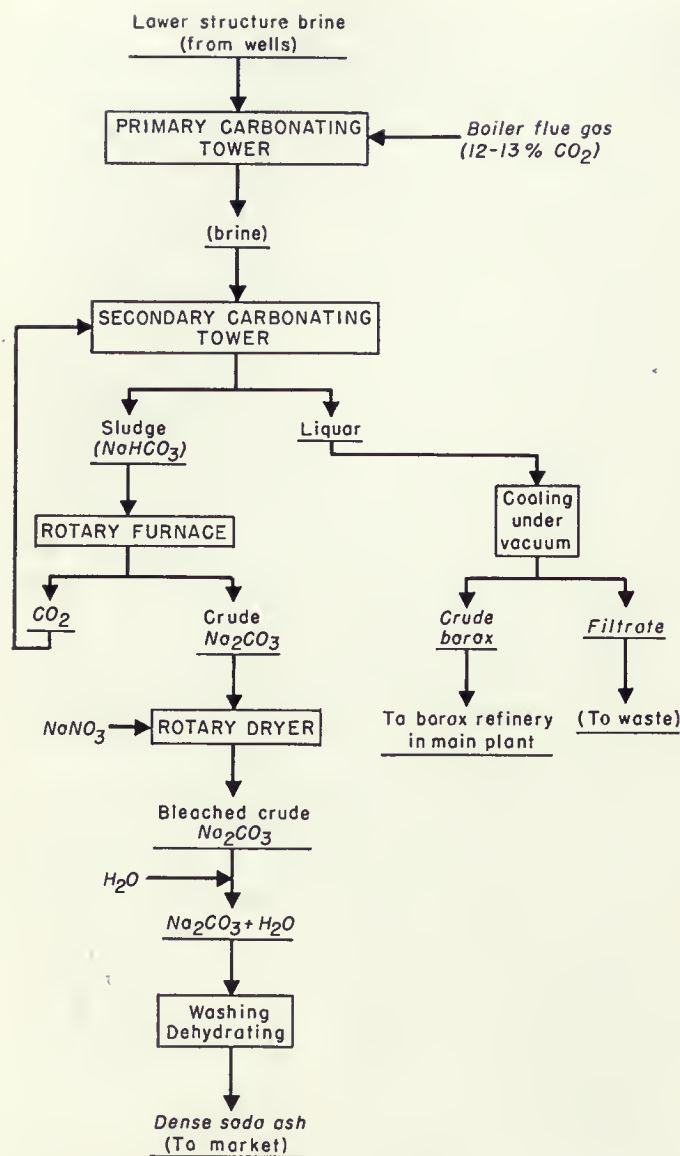


FIGURE 2. Flow sheet, carbonation plant process, American Potash & Chemical Corporation.

and borax ( $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ ) arranged in very irregular layers characterized by one salt or a group of salts. The following log of a bore hole in the central part of the lake illustrates the typical sequence (Teeple, J. E., 1929, pp. 15, 16).

0-15 feet:	Halite
15-20 feet:	Halite, hanksite, and trona
20-25 feet:	Mostly hanksite
25-40 feet:	Hanksite, halite, trona, borax
40-55 feet:	Hanksite, halite, trona, borax, and glaserite
55-65 feet:	Mostly glaserite and halite
67-70 feet:	Trona, halite, and hanksite
70-75 feet:	Trona, halite, hanksite, and borax

In other holes the surface layer of nearly pure halite is commonly found. Below the surface layer the same salts are encountered as in the example above but in different proportions.

The brines of the upper and lower crystal bodies or structures are of the same general type, but the propor-

tions of the dissolved solids differ. The most significant difference is the higher potassium content of the upper brine.

*Composition of the upper and lower structure brines of Searles Lake.*

(Ryan, J. E., 1951, p. 449, Table 1)

	Upper structure, percent	Lower structure, percent
KCl	5.08	2.94
$\text{Na}_2\text{CO}_3$	4.80	6.78
$\text{Na}_2\text{B}_4\text{O}_7$	1.63	1.96
$\text{Na}_2\text{SO}_4$	6.75	6.56
NaCl	16.06	15.51
$\text{Na}_2\text{S}$	0.08	0.38
$\text{Li}_2$	0.015	0.006
KBr	0.12	0.08
$\text{WO}_3$	0.007	0.004
$\text{I}_2$	0.003	0.002
$\text{P}_2\text{O}_5$	0.070	0.044
F	0.002	0.002

Neither the brines nor the crystal bodies contain calcium or magnesium salts, although these are among the salts that are disseminated in the impervious mud.

Owens Lake before its desiccation contained principally carbonates, sulfates, and chlorides. The lake bed now contains a porous, brine-filled crystal body similar to that at Searles Lake but with a maximum thickness of only 9 feet. Both the crystal body and brine are higher in soda content and lower in potash content than Searles Lake.

*Composition of Owens Lake brine. †*

	Summer (percent)	Winter (percent)
$\text{Na}_2\text{CO}_3$	16.62	11.98
$\text{Na}_2\text{B}_4\text{O}_7$	2.23	2.60
$\text{Na}_2\text{SO}_4$	2.32	5.04
NaCl plus KCl *	14.23	15.67

\* Average brine contains 2-3 percent KCl.

*Commercial Operations.* The commodities obtained from Owens Lake include trona or sodium sesquicarbonate, soda ash, and borax, while from Searles Lake the following are produced: potash, borax, boric acid, soda ash, salt cake, bromine, lithium carbonate, and phosphoric acid.

Salines have been produced continuously from Owens Lake since the early 1880's. The history of production can be divided into three more or less overlapping phases determined mainly by the concentration of the lake water and the methods required for treating it. The first began with the completion of the Carson and Colorado Railroad in 1884 and continued until about 1921. The Inyo Development Company evaporated lake brine in solar ponds and precipitated trona which was calcined to a rather poor grade of soda ash. This process was discontinued when the lake brine became so concentrated that the trona precipitated in the lake.

During the second phase, which lasted from 1915-37, sodium bicarbonate was made by passing carbon dioxide from lime kilns through towers containing lake brine. Sodium bicarbonate was calcined to soda ash, and the  $\text{CO}_2$  was recycled. The Natural Soda Products Company,

† May, F. H., and Leonard, M. L., The utilization of natural brines from California dry lakes for the manufacture of soda ash by carbonation: Unpublished paper presented at Am. Inst. Min. Met. Eng., southern California section meeting, Los Angeles, October 25, 1949.



the California Alkali Company, and the Inyo Chemical Company used this process.

The third and present phase began in 1935 when the concentration of the lake brine became so high that the bicarbonate no longer could be obtained in the carbonating towers. Brine is now treated by the Kuhnert carbonation process which yields sodium sesquicarbonate or trona. At present the only plant in operation is that of the Pittsburgh Plate Glass Company at Bartlett on the northwest shore of the lake.

Brine is pumped from wells sunk in the crystal body and concentrated by solar evaporation to 13 percent sodium carbonate. The concentrated brine is carbonated with flue gas in open-topped wooden towers 80 feet high. Flue gas with a carbon dioxide content of about 14 percent is compressed to 30 pounds per square inch. Trona is precipitated, partly dewatered in a thickener tank and dewatered further with centrifuges. The principal product of the plant is sodium sesquicarbonate (trona) which is prepared by drying the centrifuge cake at about 150° C. Part of the cake is calcined to soda ash in a multiple-hearth type of roaster. Borax can be recovered by chilling the centrifuge filtrate, but comparatively little borax has been produced since World War II.

Production of salines at Searles Lake started about 1873 when J. W. and D. S. Searles began to produce borax by leaching the crust of the playa and recrystallizing the salts. Five years later this operation was incorporated as the San Bernardino Borax Mining Company. Borax was produced until 1895 when the Pacific Coast Borax Company, which owned rich colemanite deposits near Calico, San Bernardino County, bought the property.

About 1908 the California Trona Company was incorporated for the purpose of producing soda ash both from the lake brine and from the reefs of trona on the east side of the lake. This operation failed in 1909. The receiver continued development and kept the property intact by performing the necessary assessment work.

The shortage of potash that became acute during World War I began to develop in 1910. The presence of potash in Searles Lake was announced to the press in March 1912 after E. E. Free of the United States Bureau of Soils and H. S. Gale had collected and analyzed representative brine samples. This announcement and a report prepared and published by the United States Geological Survey created a lively interest in Searles Lake. A period of claim jumping followed that clouded the title of the California Trona Company to its Searles Lake property. In February 1913 the United States Government withdrew from public entry the saline lands of Searles Lake, but in 1916 the California Trona Company obtained a clear title to its claims. Subsequently its successor, the American Trona Corporation, obtained patented claims in the north-central part of the lake.

The American Trona Corporation completed a plant in 1914 which was to recover sodium carbonate and potassium chloride. The operation was unsuccessful, and commercial operations did not begin until September 1916 after the plant had been completely rebuilt. Several other companies built experimental plants; but only one, in addition to the American Trona Corporation, became a producer. This plant, owned jointly by the

Pacific Coast Borax Company and the Solvay Process Company, operated at Borosolvay from 1916 to 1920. A low grade of potash was produced at high cost.

After foreign potash became available again, potash from Searles Lake was no longer salable. The plant at Borosolvay was shut down, but the American Trona Corporation initiated an intensive research program that enabled it to reduce costs and improve the quality of its products. Reorganized as the American Potash & Chemical Corporation, the company is now a major producer of chemicals. Early in World War II it was discovered that over 90 percent of the stock was owned by German nationals. These shares were seized by the Alien Property Custodian which held them during the remainder of the war. On March 27, 1946, the company was returned to private control. The seized shares were bought by a group of investment bankers for resale.

The American Potash & Chemical Corporation produces potassium salts, borax, boric acid, sodium carbonate, sodium sulfate, bromine, lithium carbonate, and phosphoric acid in two relatively independent operations. The main plant process treats the upper brine, while the lower brine is treated separately in the carbonation plant process.

In the main plant process a mixture of brine from the upper crystal body and recycled mother liquor, called mother liquor number 2, is concentrated in triple effect evaporators equipped with external heat exchangers. The liquor flows counter to the flow of heat; that is, the liquor enters the third effect pan and is transferred from it to the second effect pan and then to the first effect pan. During the evaporation common salt, burkeite ( $2\text{Na}_2\text{SO}_4 \cdot \text{Na}_2\text{CO}_3$ ), and dilithium sodium phosphate ( $\text{Li}_2\text{NaPO}_4$ ) crystallize abundantly in all three pans and are continuously withdrawn. These salts, after being washed free of entrained liquor, are separated into a coarse fraction high in sodium chloride and a fine fraction containing most of the burkeite and lithium salt. The sodium chloride is discarded and sent back to the lake at the rate of 2,500 tons per day.

The burkeite-rich fraction, the feed for the soda products process, is mixed with carbonate-rich end liquors and leached of free sodium carbonate in a cold saturator tank. Additional free carbonate is obtained by treating the burkeite with sodium chloride in a hot saturator tank. Both saturator tanks discharge into 60-foot Dorr thickeners, the overflow from which, rich in free carbonate, is the feed for the sodium carbonate refinery. Salt is removed by chilling, and further chilling precipitates sal soda ( $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ ) which, after dehydrating and additional refining steps, is sold as soda ash.

The underflow from the 60-foot Dorr thickeners is burkeite and entrained dilithium sodium phosphate. This mixture is dissolved to yield a burkeite solution containing dilithium sodium phosphate in suspension. Heat liberated in dissolving the burkeite is removed in a cooling tower. The burkeite solution goes to the lithium flotation plant where the lithium salt is removed for processing as described in the section on lithium in this bulletin. The clarified burkeite solution is sent to the sodium recovery section where a portion of the sulfate is extracted as glauber salt ( $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ ) by cooling to 78° F. and converted to anhydrous sodium sulfate by treatment with sodium chloride. Much of the sodium sulfate re-



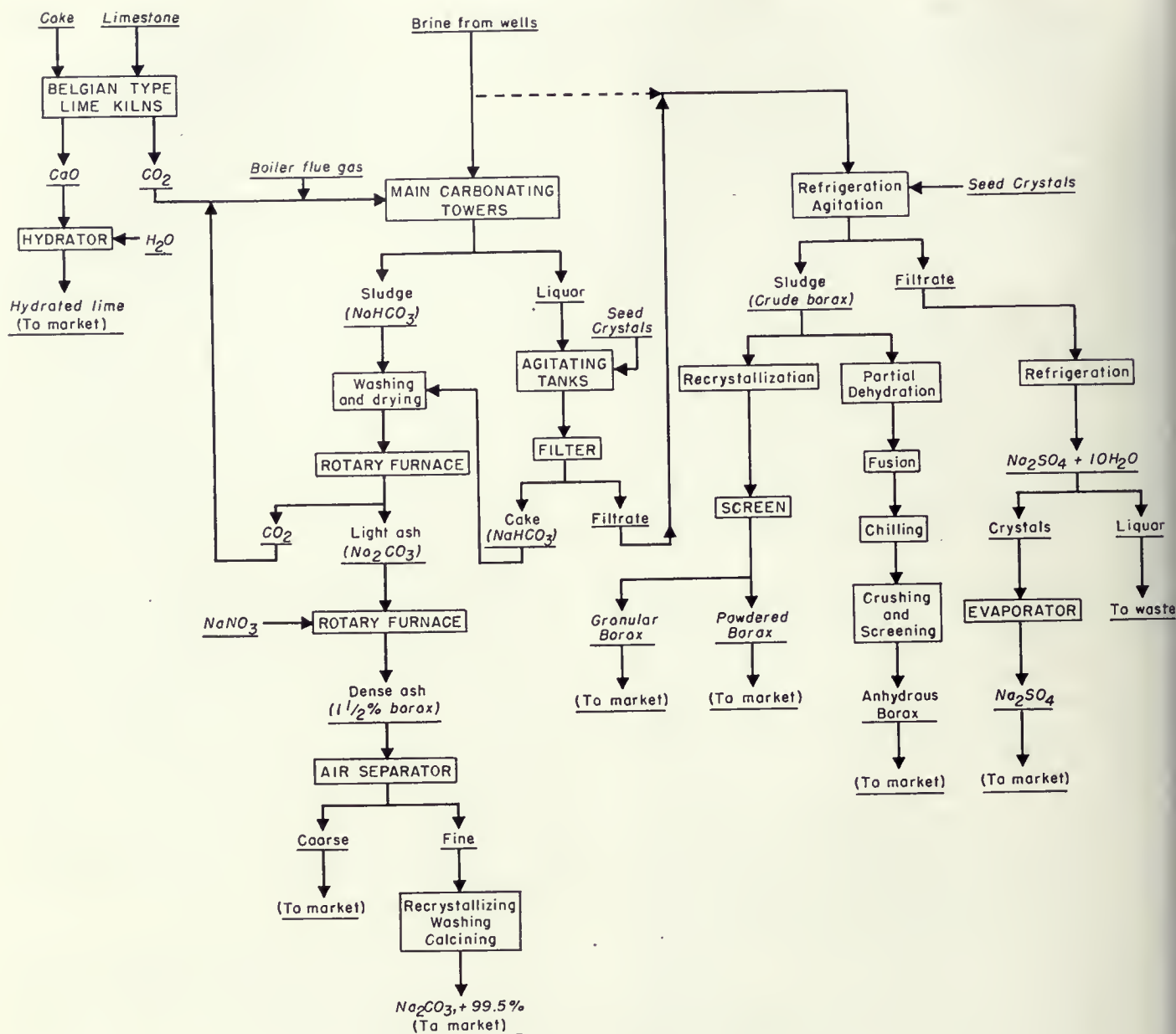


FIGURE 3. Flow sheet, West End Chemical Company.

maining in the glauber salt filtrate is precipitated by chilling and treatment with additional sodium chloride. The crude sodium sulfate is refined; and the end liquor, rich in sodium carbonate, is returned to the cold saturator.

The feed for the potash and borax recovery operations is the liquor drawn from the first effect pans of the main evaporators, nearly saturated with potassium chloride and at about 250° F. Potassium chloride is crystallized by chilling the hot liquor to 100° F. in three-stage vacuum coolers. In order to keep all salts except potassium chloride in solution, the liquor is first diluted. The chilled liquor is supersaturated with sodium tetraborate pentahydrate ( $\text{Na}_2\text{B}_4\text{O}_7 \cdot 5\text{H}_2\text{O}$ ), but because the chilling is done rapidly with a minimum of agitation, the crude potassium chloride contains but a small amount of borate.

The crude potassium chloride is recovered by filtration; and the filtrate, called mother liquor number one, is forwarded to the borax recovery section.

Much of the crude potassium chloride, after washing and drying, is sold as agricultural potash. A portion is treated with burkeite to produce potassium sulfate for agricultural use, and another portion is refined by recrystallization for chemical use. Bromine is recovered from the potassium chloride solution with Kubierschky towers.

In the borax recovery section,  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 5\text{H}_2\text{O}$  is crystallized from the mother liquor number one by agitation and the use of seed crystals. The end liquor, called mother liquor number 2, is returned to the main evaporating pans. Some of the crude tetraborate pentahydrate, after washing and drying, is sold; but much of



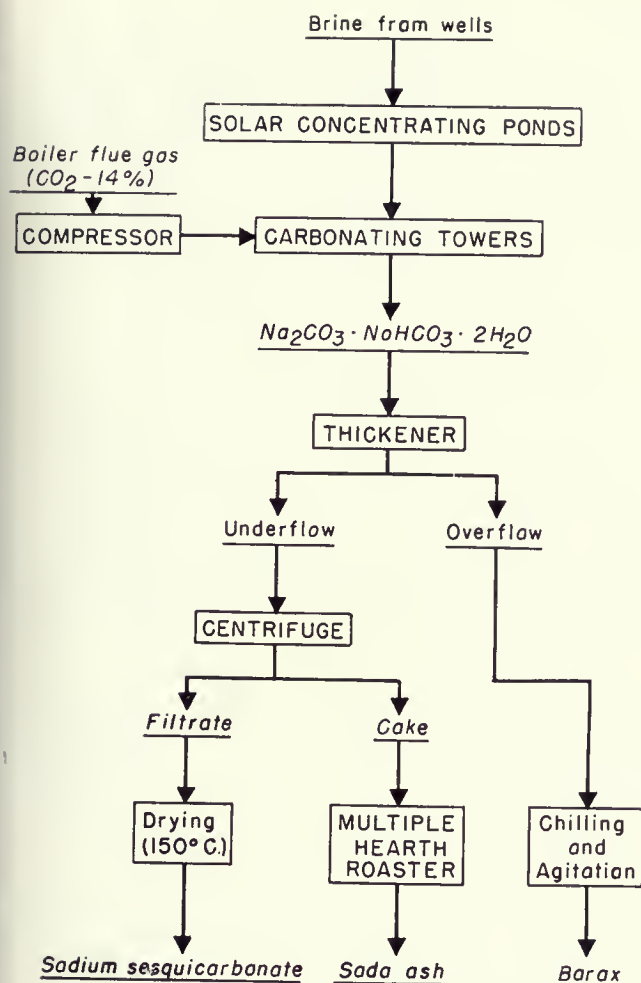


FIGURE 4. Flow sheet, Columbia Chemical Division.

it is refined and recrystallized as tetraborate pentahydrate or borax (tetraborate decahydrate). Some of the refined borax is treated with sulfuric acid to form boric acid, and some is fused to form anhydrous borax.

In the carbonation plant (May, F. H., and Leonardi, M. L., 1949) soda ash is produced from the lower structure brine by carbonation with boiler flue gas. Carbonation is carried out in two stages and in towers 14 feet in diameter and 50 feet tall. Flue gas containing 12 to 13 percent carbon dioxide and at a pressure of 15 pounds per square inch is admitted to the primary towers in which the brine is partially carbonated. The temperature within the towers is controlled by regulating the temperature of the flue gas admitted. Brine from the base of the primary towers is admitted to the tops of the secondary towers in which the carbonation is completed with rich, recycled carbon dioxide gas. Precipitated sodium bicarbonate sludge is withdrawn, thickened, washed, and dried. Carbonation also releases hydrogen sulfide from the sulfide-rich lower structure brine. Corrosion resistant materials are used in the carbonation plant, and the waste gases from the carbonating towers must be treated to remove poisonous gases before they are released into the atmosphere.

The sodium bicarbonate is calcined in a revolving externally heated cylinder 8 feet in diameter and 80 feet long. A heavy chain within the cylinder and fastened at the ends drags on the bottom. The charge is stirred, and the formation of scale on the walls is prevented. The calciner gas, consisting of carbon dioxide and water vapor, is washed, compressed, and delivered to the secondary towers. The fully decomposed bicarbonate or soda ash is withdrawn through a gas-tight chute and bleached with previously added sodium nitrate in a rotary drier.

This crude soda ash, which contains 2 to 3 percent of sodium sulfate, sodium chloride, and borax, is treated with water. The soda ash is converted to sodium carbonate monohydrate (Na<sub>2</sub>CO<sub>3</sub> · H<sub>2</sub>O), and the impurities are washed out. The purified monohydrate is then fully dehydrated by drying at 300° to 400° F. The final product is a dense soda ash containing more than 99.6 percent Na<sub>2</sub>CO<sub>3</sub>.

The West End Chemical Company (Wiseman, J. V., and Blackmun, L. A., 1951) produces soda ash, borax, and sodium sulfate from a mixture of the upper and lower structure brines by a process similar to that used in the carbonation plant at the American Potash & Chemical Corporation. The brine is carbonated in 72 wooden towers, each 75 feet high and 5 feet in diameter. A portion of the gas used for carbonation is boiler flue gas, and the remainder is obtained from limestone quarried north of Searles Lake, that is burned in vertical kilns with metallurgical coke obtained in Alabama. The by-product quicklime is hydrated and sold as chemical lime.

After the sodium bicarbonate from the towers is washed and dried, it is calcined in an externally fired rotary furnace. The carbon dioxide evolved is then recycled. The calciner product is light-weight soda ash colored brown by organic matter present in the brine. The light ash is whitened by adding a small amount of sodium nitrate and heating to a temperature close to the fusion point. The product is dense soda ash weighing about 55 pounds per cubic foot. At this point the soda ash contains about 1½ percent Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> which was precipitated with the bicarbonate in the towers. For some consumers, particularly glass manufacturers, the borax-bearing soda ash is desirable; but for other uses a high purity soda ash is prepared by recrystallization of the monohydrate followed by washing and calcining.

After the bicarbonate sludge has been withdrawn from the towers, some additional bicarbonate is recovered from the liquor by agitation and the use of seed crystals.

In the borax recovery operation the carbonate-free brine is mixed with raw lake brine to adjust the pH. By means of ammonia refrigeration the brine is cooled to 60° F. and agitated in a series of large tanks. Seed crystals are added, and crude borax precipitates from the solution. Some of the crude borax is refined by recrystallization, and the remainder is converted to anhydrous borax by partial dehydration followed by fusion. The fused borax is chilled on a metal drum; and after it has cooled, it is crushed and sized.

Beginning in July 1955 the West End Chemical Company has been producing sodium sulfate from the efflu-



ent from the borax recovery operation. The liquor is further chilled to 45° F., and crystals of  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  form. These crystals are recovered and converted to anhydrous sodium sulfate in a special evaporator (Chem. Eng., 1955).

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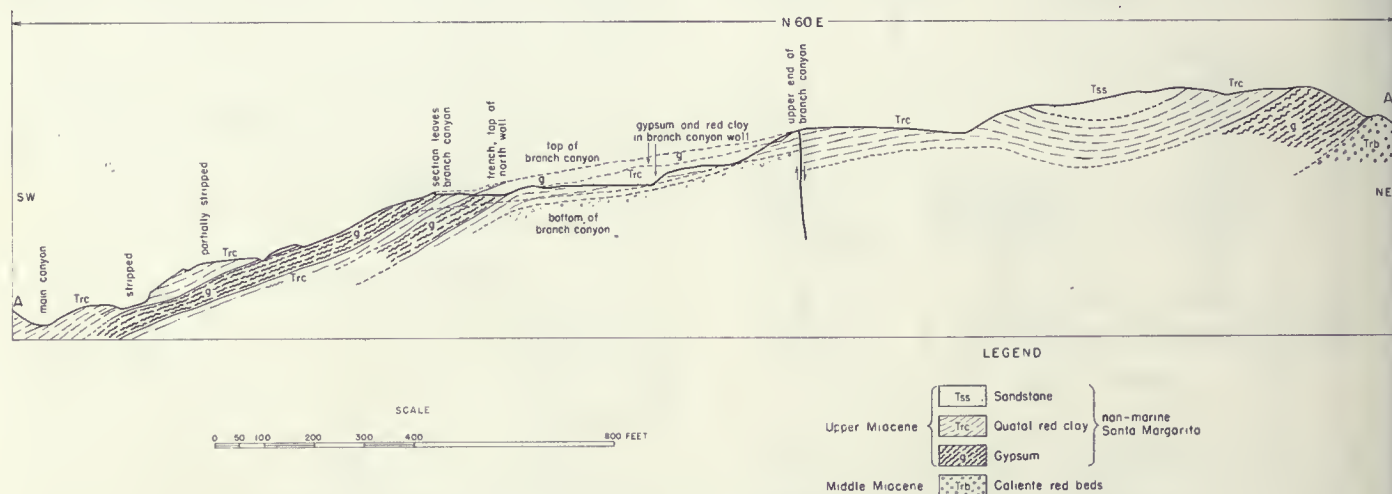


FIGURE 5. Geologic structure section through the Quatal Canyon gypsum deposit. Reprinted from California Division of Mines Bulletin 163, p. 36.



# SALT

BY WILLIAM E. VER PLANCK

Common salt (NaCl) is a basic material for human existence as well as for the chemical industry. The state's 1953 production of 1,123,365 tons was valued at \$6,263,059. The California salt industry is centered on the southeast shore of San Francisco Bay where the Leslie Salt Co. obtains salt from sea water in one of the world's largest solar evaporation plants. About 25 percent of the total production is obtained at other points on the California coast and from certain dry lakes in the California desert.

**Geologic Occurrence.** Halite, the natural sodium chloride, most commonly crystallizes as cubes or in granular masses. Halite is among the most soluble of the common minerals. Salt, because of its great solubility, is present in almost all natural water. Sea water is essentially a 3.5 percent solution of several salts of which a little more than 77 percent is sodium chloride. The waters of some undrained desert basins are high in salt, while salt springs and wells are to be found in regions having humid climates as well as in the desert.

Most deposits of rock salt have resulted from the evaporation of saline water. In California certain dry lakes contain beds of halite or mixtures of halite and other saline minerals. Most of these salt beds or crystal bodies are in contact with concentrated mother liquor with which they are in chemical equilibrium. Dry lakes also contain salt in the form of efflorescent, salty crusts or of halite crystals disseminated in mud. Some deposits of halite that are interbedded with folded and faulted sediments are believed to be older dry lake deposits.

Exposed rock salt can exist only under arid climatic conditions, but under favorable circumstances salt deposits have been buried and protected from solution. The world's largest reserves of rock salt are in the form of beds associated with sedimentary formations of nearly all geologic ages. Salt beds of the Salina formation of New York and Michigan, the Permian beds of Texas and New Mexico, and other great salt-bearing formations are as much as several hundred feet thick over areas of more than 100 square miles. Other large salt deposits are in the form of "domes" which exist as plug-shaped masses that intrude the enclosing sediments. No salt domes have been found in California.

**Salt from the Solar Evaporation of Sea Water.** Solar evaporation is the only method used for producing salt from sea water on a commercial scale, and even this method is feasible at only a few localities. Primarily here must be sufficient evaporation and enough space available to produce a crop of salt large enough to handle economically. Of equal importance is the proximity of salt-consuming industries.

Suitable land is of limited occurrence and highly valued. With a maximum yield in the San Francisco Bay area of 40 tons per acre, thousands of acres must be in production. Small salt works of less than 200 acres are in operation today, but to obtain the maximum advantage from mechanized equipment, a single salt works should contain at least 5,000 acres. The land should be flat and close to sea level and it should be impervious to prevent loss of brine. Salt marshes most

nearly fulfill these requirements. Today the salt industry must compete for marsh land with expanding industries and communities. It is becoming increasingly feasible to reclaim swamp land by draining and filling, and along the California coast large areas that could once have been used for salt production are now covered with houses or industrial plants. The solar salt industry at Long Beach passed out of existence in 1946 when the land was filled in.

Rainfall and relative humidity must be low during a substantial part of the year. Net evaporation in San Francisco Bay is 34 to 43 inches per year.

The south end of San Francisco Bay combines the factors essential for salt production. The largest producer is the Leslie Salt Co. with plant headquarters in Newark and nearly 30,000 acres in production in Alameda, Santa Clara, and San Mateo Counties. Four separate crude salt plants are in operation, and a fifth plant is under construction on the north shore of San Pablo Bay. Practically all grades of crude and refined salt are manufactured. Other much smaller sea water plants that produce crude salt only are operated by the American Salt Company and Oliver Brothers Salt Company at Mount Eden, Alameda County; E. C. Vierra near Moss Landing, Monterey County; and the Western Salt Company at Chula Vista, San Diego County, and Newport Bay, Orange County.

The process of obtaining salt from sea water is essentially fractional crystallization. Sea water passes through a series of outer or concentrating ponds in which, by the action of sun and wind, it is evaporated to the point of saturation with respect to sodium chloride; and the slightly soluble carbonates and gypsum are precipitated. The saturated brine or pickle has a specific gravity of 25.6° Be., and its volume has been reduced to about 10 percent of the volume of sea water taken in. Pickle is transferred to a separate group of ponds called crystallizing ponds where continuing evap-

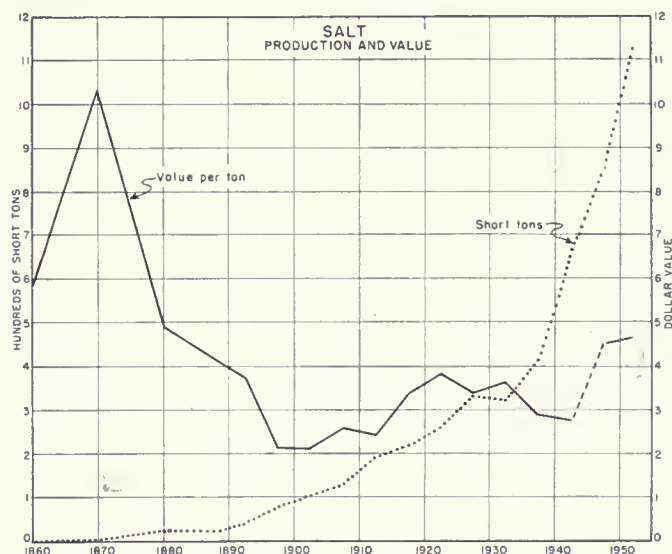


FIGURE 1. Chart showing the production of salt in California, 1860-1953.





FIGURE 2. Aerial photograph showing Leslie Salt Co. plant and Morton Salt Co. plant, Newark, Alameda County. The California salt industry is centered on the southeast shore of San Francisco Bay where Leslie Salt Co. operates one of the world's largest solar evaporation plants. Practically all grades of crude, kiln dried, and



oration causes salt to form. In order to avoid the precipitation of the very soluble magnesium salts the crystallizing ponds are drained and refilled with fresh pickle when the specific gravity reaches  $29^{\circ}$  to  $30^{\circ}$  Be. The larger plants sell the mother liquor or bittern to chemical plants for the recovery of magnesium compounds, bromine and gypsum.

Concentrating pond systems contain about 10 ponds, each up to 100 acres or even 500 acres in size, arranged in series. They have natural bottoms and are formed by levees built of mud that usually follow physical features such as sloughs. As far as possible concentrating ponds are built between the high and low tide marks so that they can be filled by means of tidal gates and to minimize pumping in the transfer of brine between ponds. Crystallizing ponds have a total area of 6 to 8 percent of the crystallizing ponds and are provided with pumps and ditches for rapid filling and draining. Individual ponds range from 10 acres or less to 50 or 60 acres in size. To facilitate harvesting they are rectangular and have flat bottoms.

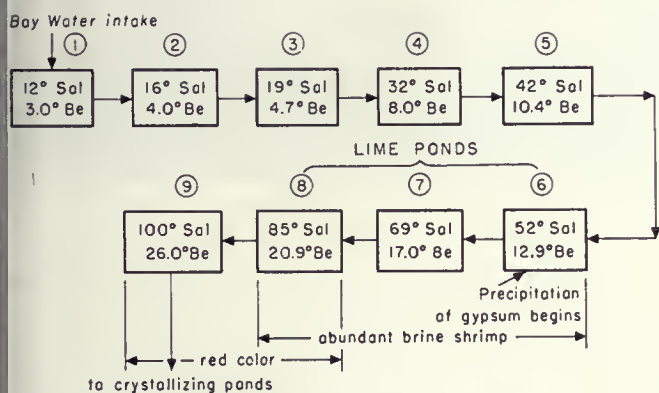


FIGURE 3. Diagram illustrating the progress of brine concentration.

Sea water is taken in from April or May through October or November, and about a year is required for it to reach the crystallizing ponds. During the winter when net evaporation is negligible the plants are dormant. Pickle is available for the crystallizing ponds the following spring because rain water lies on the surface of strong brine and does not mix with it appreciably.

Once a year the crystallizing ponds are drained and harvested one at a time. On San Francisco Bay all the ponds are harvested in the fall, and they are not refilled until spring. In southern California a small force of men harvests salt during most of the evaporating season. Ponds are refilled as soon as they have been harvested, and any salt that subsequently forms is left in the ponds until the following year. All the California plants use mechanized methods. The Leslie Salt Co. has 6 crawler tread mounted harvesting machines, each with a capacity of 150 tons of salt per hour. Salt is broken free with picks mounted on a horizontal revolving shaft and thrown onto a short drag chain conveyor that discharges into dump cars running on portable rack laid on the salt. Some 75 miles of narrow gauge rack serve the four Leslie plants. The Western Salt Company harvests with dragline scrapers, and the other sea water plants use still other methods. Immediately



FIGURE 4. Photo showing crystallizing ponds, Western Salt Company, Chula Vista, San Diego County. Seawater passes through a series of concentrating ponds in which the water evaporates and becomes saturated with salt. The saturated brine or pickle is then transferred to the crystallizing ponds where continuing evaporation causes the crystallization of salt. From 8 to 10 inches of salt forms during the evaporating season.

after harvesting, the salt receives one or more washes with strong brine and a final wash with a small amount of fresh water. The salt is stored in the open.

*Salt from Terrestrial Brines.* Solar evaporation is applicable to many terrestrial brines, although differences in brine composition and concentration usually require modification of the methods used by the sea water plants. With the strong brines found in many places in the desert, the concentrating ponds may be reduced or eliminated; and if sodium chloride forms a high proportion of the dissolved solids, the amount of bittern is small. Terrestrial brines to which solar evaporation is applicable are likely to be higher in sulfate and lower in magnesium than sea water. The solubility of sodium sulfate is greatly influenced by temperature; and at the temperatures that occur in the California deserts



FIGURE 5. Photo showing dragline loading cars with salt, Western Salt Company. Once a year the crystallizing ponds are drained. The salt is excavated with a dragline and loaded into cars that run on temporary track laid in the ponds.





FIGURE 6. Photo showing a harvesting machine in operation, Leslie Salt Co. Revolving picks mounted on the machine lift the salt and throw it onto a short drag chain conveyor that discharges into dump cars. *Photo courtesy Leslie Salt Co.*

in winter, it is less than that of sodium chloride. Consequently, if the brine contains much sodium sulfate, a solar evaporation plant cannot be operated in winter.

Salton Sea contains sodium chloride-sulfate brine of about the same salinity as sea water. The largest of several plants there, the Imperial Salt Works near Niland, operated from 1935 through 1946. The process used was almost identical with that of the sea water plants except for the production of sodium sulfate bittern. In addition, small tonnages of salt have been produced by the solar evaporation of spring and well brines in Surprise Valley, Modoc County (1912-41), near Suisun, Solano County (1907-19), and near Sites, Colusa County (1895-1908).

**Salt From Dry Lakes.** The recovery of salt is most feasible from dry lakes containing chloride or chloride-sulfate brine. Bristol Lake, Cadiz Lake, Danby Lake, and Dale Lake in San Bernardino County contain brines of this type in which the sulfate content ranges from zero to more than 15 percent of the dissolved solids. Bristol Lake contains in its central part a series of salt and clay beds at least 1,000 feet thick. A meager amount of saturated sodium-calcium chloride brine permeates the upper salt beds, but sulfates are absent except along the lake margins. For many years the California Salt Company and its predecessors have quarried salt from the top bed. The recovery of calcium chloride is described in another section of this bulletin. Cadiz Lake, the least known of the four, has yielded no production. The brine is of the sodium-calcium chloride type, but with a lower calcium content than that of Bristol Lake.

Both gypsum and salt beds have been reported at this locality.

Danby Lake contains large near-surface beds of salt, much of which is porous and permeated with concentrated sodium chloride brine with a minor sulfate content. The Danby Lake brine does not yield calcium chloride when it is evaporated. Although the salt beds contain only minor amounts of sulfate, the clay contains disseminated crystals of gypsum, mirabilite ( $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ ), and halite. Salt has been quarried by the Crystal Salt Company in the late 19th century and by J. W. Reeder from 1934 to 1942. More recently the Metropolitan Water District of Southern California explored the lake with bore holes and conducted solar evaporation tests on the brine. In Dale Lake the proportion of sulfate to chloride is substantial, and up to the end of 1948 both salt and sodium sulfate were produced. The dormant Dale Lake operation is described in the section on sodium sulfate in this bulletin.

Several other desert basins in California contain salt deposits and chloride-sulfate brines. Koehn Lake, near Saltdale, Kern County, yields salt although neither salt beds nor subsurface brine are known. Production is from surface brine formed by rain water that collects in the lake and dissolves the efflorescent, saline crust. The brine is allowed to approach saturation before it is run into solar evaporation ponds. The amount of bittern is small.

In Death Valley the floor for an area of 45 miles long and as much as 4 miles wide is covered with a salt crust as much as 5 feet thick. A few widely scattered bore holes have penetrated salt and clay beds to a depth of at least 600 feet and have encountered saturated sodium chloride-sulfate brines. Some of the deep salt



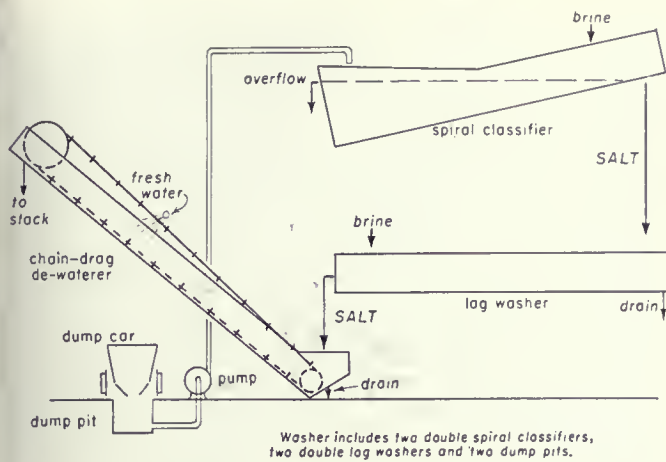


FIGURE 7. Flowsheet of the washer, Newark No. 2 crude salt plant, Leslie Salt Co.

beds are as much as 15 feet thick. Salt was produced from the crust near Badwater in 1942.

Saline Valley, Inyo County, contains a crust like that in Death Valley, but much smaller in area. From 1911 to 1930 salt was obtained by scraping the crust and also by evaporating brine made by dissolving the crust in fresh water, and in 1954 the Saline Valley Development Company harvested and stockpiled about 2,000 tons of salt.

At Searles Lake the Pacific Salt and Chemical Company produces salt from fee holdings of the American Potash & Chemical Corporation. Although the crystal body of Searles Lake is composed largely of complex borates, carbonates, and sulfates, the upper 10 to 15 feet is sodium chloride of high purity. Stripping is not necessary, and salt scraped from the surface is shipped without treatment. Owens Lake, Mono Lake, and Borax Lake are unfavorable sources of salt. Not only does salt form a lower proportion of the salines than it does in the chloride lakes, but the brines yield trona ( $\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$ ) rather than salt upon evaporation.

**Avawatz Mountains Deposits.** The only known Tertiary deposits of salt in California are those in the north-

ern foothills of the Avawatz Mountains, San Bernardino County. Salt, gypsum, and celestite occur in Pliocene (?) lake beds in the Death Valley fault zone near its junction with the Garlock fault zone. The structure is complex, and the stratigraphic succession has not been positively determined. Two nearly parallel strips of lake beds bounded by brecciated pre-Tertiary rocks extend northwestward along the mountain front for about 9 miles. The lake beds consist of a salt-bearing unit, a gypsum-bearing unit, and saline-free units that enclose the salt and gypsum beds. The salt-bearing unit consists of 100 to 600 feet of reddish brown clay and a varying thickness of massive, coarsely crystalline rock salt. In most places the salt is concealed by residual clay. Salt deposits in the Boston-Valley claims were explored by Basic Magnesium Incorporated during 1941 and 1942 with diamond drilling and some shaft and tunnel work. An area of less than 2 acres in the southern strip of lake beds between Denning Spring Wash and Cave Spring Wash was found to contain 1,300,000 tons of salt over 92 percent pure. Other salt deposits in the vicinity, including the one in Salt Basin, have not been explored but probably contain large tonnages.

**Uses and Marketing.** Common salt is of economic value principally because (1) as an industrial chemical, it is the raw material from which most sodium and chlorine compounds are made; (2) it is an essential ingredient in the diets of men and animals; (3) as an antiseptic, it is used in the preservation of food, especially meat and fish, and in the preparation of hides for tanning; and (4) the saturated solution has a relatively low freezing point ( $-4^\circ \text{F.}$ ).

As an industrial chemical, salt is the source of most of the chlorine and much of the caustic soda produced in the United States. These commodities are manufactured by the electrolysis of a sodium chloride solution. The electrolysis of fused sodium chloride yields sodium metal and chlorine. In addition, salt is used in the manufacture of soap and plays a part in the softening of water by the zeolite process. The ammonia-soda process for the manufacture of soda ash consumes more than half of all the salt used in the United States; but on the West Coast, soda ash is produced from natural sources.

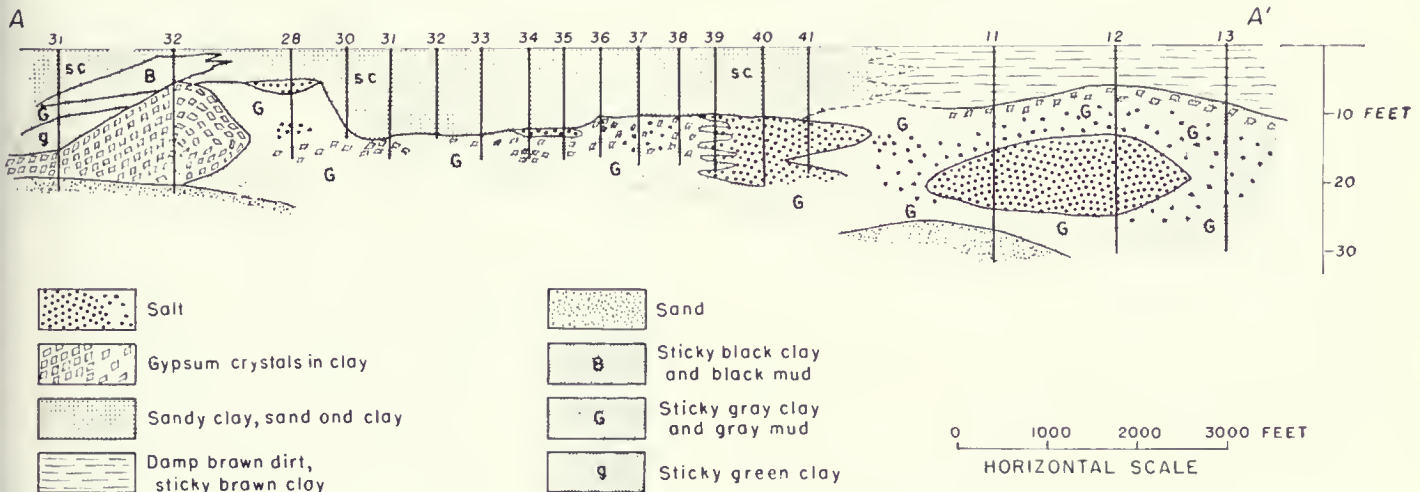


FIGURE 8. Geologic section through the northwest portion of Danby Lake, San Bernardino County.





FIGURE 9. Drilling salt at Bristol Lake, California Salt Company. Bristol Lake contains a salt bed 5 feet thick beneath a shallow overburden of clay. The drill stands on salt exposed in a long pit formed by removing the overburden with a dragline. Holes are drilled with a gasoline-powered auger and blasted with 30 percent dynamite.

Because of the low freezing point of its solution, much salt is consumed in the salt-ice mixture that is used for the cooling of railroad refrigerator cars. Salt is also used for ice control, especially around railroad switches and crossings. A salt solution is used as the cooling medium by many ice plants.

Three general types of salt are marketed in California: crude salt, kiln dried or semi-refined, and vacuum refined salt. Crude salt produced from sea water contains 99.4 percent NaCl, but some desert salt is of lower grade. Kiln dried salt is a sterile, moisture-free product prepared by heating crude salt to a temperature of about 365° F. in a rotary kiln. It contains about 99.8 percent NaCl. The salt dust produced in the processing of kiln dried salt is collected and made into blocks with hydraulic presses. Vacuum refined salt, the purest type commercially available, contains over 99.95 percent NaCl. It is prepared from chemically treated brine made by dissolving crude salt in fresh water. The treated brine is evaporated by boiling with steam in closed, partially evacuated vessels called pans; and the salt that crystallizes is continuously removed for drying and sizing. Approximately 20 percent of the California production is kiln dried salt, salt blocks, and vacuum refined salt. With the exception of a comparatively small output of kiln

dried salt at Saltdale, Kern County, these types are produced in the San Francisco Bay area only. Roughly half of the salt produced in California is shipped to destinations outside of the state.

Crude salt sold in bulk to the chlorine-caustic industry accounts for between 45 and 50 percent of the California salt production. Salt from San Francisco Bay is sent by sea to three plants in the Pacific Northwest and by rail to a fourth plant in Contra Costa County. A fifth plant, in southern Nevada, obtains salt from the Bristol Lake deposit, San Bernardino County. The remainder of the California salt output is used for a host of purposes. Zeolite water softening, refrigeration, and food processing each consume between 10 and 15 percent of the total; livestock feeding requires nearly 7 percent; and a minor proportion is used for purposes such as the manufacture of soap, synthetic rubber, and in the preparation of hides and leather. Domestic uses, including table salt, require less than 3 percent of the total. Vacuum salt is used for table salt and in the preparation of food. Kiln dried salt and salt blocks are used for stock feeding, and kiln dried salt also is used for industrial purposes. Because of its low moisture content and freedom from caking, many consumers prefer it to crude salt.

With few exceptions, salt is sold on the Pacific coast on f.o.b. producer's plant basis. Typical carload prices f.o.b. plants in the San Francisco area in 1954 were as follows:

Undried, stack run or half ground	
Bulk	\$6.40 per ton
100 pound paper bag	13.40 per ton
125 pound burlap bag	14.60 per ton
Kiln dried, mill run, coarse, extra coarse	
Bulk (mill run not available in bulk)	9.20 per ton
100 pound paper bag	16.20 per ton
Vacuum table	
Bulk	16.00 per ton
100 pound paper bag	23.00 per ton

The price at plants close to Los Angeles is higher than the published prices in the San Francisco area, but for the more remote desert plants it is considerably less.

Freight rates amount to a substantial portion of the f.o.b. plant price. The following rail freight rates were in effect in 1954:

Origin	Destination (rate per ton inc. 3 percent federal transportation tax)				
	San Francisco	Los Angeles	Seattle	Portland	Las Vegas
Newark	\$1.42	\$7.83	\$8.86	\$7.42	\$12.15
San Diego	—	2.76	—	—	—
Salts					
(Bristol Lake)	6.80	4.33	12.57	11.12	4.15
Trona					
(Searles Lake)	10.64	4.26	16.83	15.38	—
Salt Lake City, Utah	10.51	9.89	14.83	14.42	9.89

Salt produced in southern California is marketed in the Los Angeles area for purposes such as water softening, refrigeration, and stock feeding. Very little of it is sold north of Los Angeles.

Another method of marketing salt is the long term contract between the producer and a large scale consumer such as a chlorine-caustic manufacturer. Only a handful of such contracts are outstanding in California, but they account for a substantial portion of the total salt production. The terms of these contracts are seldom revealed. Large consumers, particularly the chlorine-caus-





FIGURE 10. Photo showing Saltdale plant of Long Beach Salt Company, Kern County. Salt produced by the solar evaporation of the surface brine of Koehn Lake is brought to the plant in narrow-gauge cars where it is crushed and screened. Some is sold as crude salt and some is made into semi-refined salt in a kiln drier.

tic industry, must have a dependable supply of low cost salt. The San Francisco Bay salt industry and the Pacific Coast chlorine-caustic industry are mutually interdependent, and neither could have achieved its present status without the other. Salt from inland deposits cannot be brought to San Francisco or placed on ships for transport to Oregon and Washington at prices that these industrial consumers could pay and remain in business.

*History of Production.* The earliest white settlers in the San Francisco Bay region obtained salt from natural deposits that formed in tide pools on the marshes along the Alameda County shore. The salt industry of California may be said to have started in 1856 when a small quantity of this salt was placed on the market. The natural salt was of poor quality, and its harvest was uncertain. It was a simple step to increase the yield by building levees to enlarge the natural tide pools. Perhaps the discovery of the Comstock Lode, Washoe County, Nevada, was the greatest single stimulus to the California salt industry. Salt was one of the chemicals used in the Washoe process for treating silver ores, and until 1862 all the salt used was shipped from San Francisco to Virginia City where it sold for \$150 a ton. With the discovery of salt deposits in Nevada, shipments from San Francisco declined, but metallurgy remained an important market for salt throughout the 19th century.

The first attempt to improve the quality of the natural salt was made in 1862 by John Quigley who built a plant near Alvarado. Plummer Brothers' Crystal Salt Works was built in 1864 near Newark, and the American Salt Company, which is still in operation, was founded in 1865. By 1868 seventeen plants were in operation in Alameda County. These pioneer salt producers soon developed the salt-making technique that is used in principle today. The quality of the salt produced improved, and by 1880 imports of crude salt declined.

Throughout the 19th century the plants, with few exceptions, were small family enterprises, some of which comprised as little as 20 acres operated by a single man. Even as late as 1900, when the salt production of Alameda County had nearly reached 100,000 tons a year,

only four plants reported outputs of 10,000 tons or more.

The largest of the 19th century plants was that of the Union Pacific Salt Company. In 1882 it occupied 1200 acres of marsh land and employed 80 men. It contained 5 concentrating ponds and a large number of crystallizing ponds 6 to 8 acres in size, many of which were floored with boards. In harvesting, the salt was first shoveled into small piles and then placed in stacks on dry ground where it remained through one rainy season. Table salt was evaporated in elevated wooden pans.

Eighteen producers reported production in 1900. Corrosion and maintenance of the small plants that were constructed of inferior materials contributed to high operating costs, while lack of capital and volume of business discouraged investment in modern equipment. Most of these small plants adjoined one another so that a combining of their operations was practical. The series of events that eventually led to the consolidation of nearly all the Bay area's salt-producing capacity in the hands of one organization began with the founding of three new salt producers. They were the California Salt Company, formed in 1901; the Continental Salt and Chemical Company, organized in 1900; and the Leslie Salt Refining Company, established in 1901.

The California Salt Company built a new plant near Alvarado on land where salt had never been produced before, and it also acquired existing plants in the Alvar-

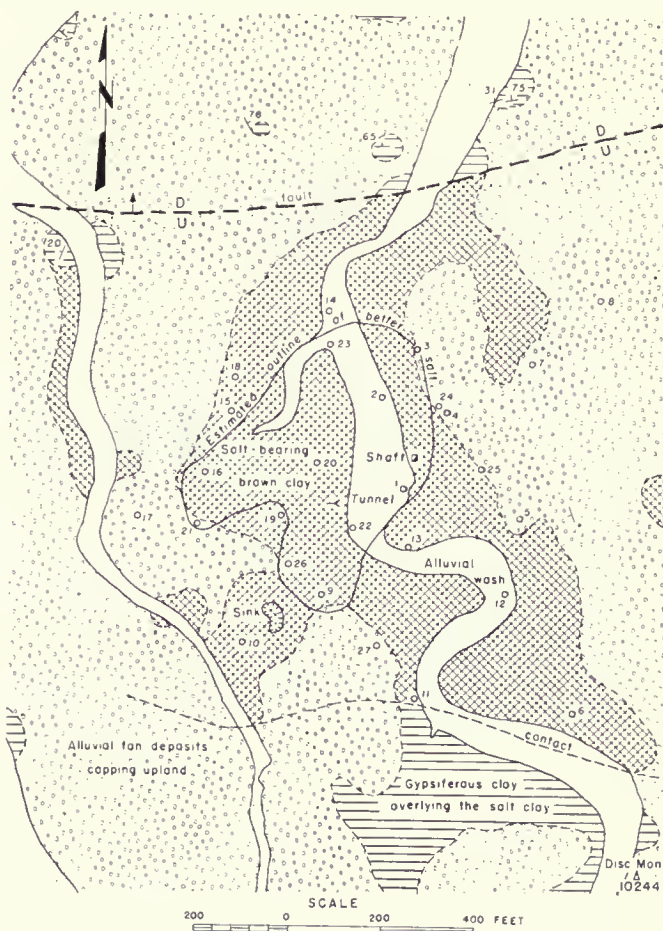


FIGURE 11. Geologic map of a portion of the Boston-Valley claims, Avawatz Mountains, San Bernardino County.



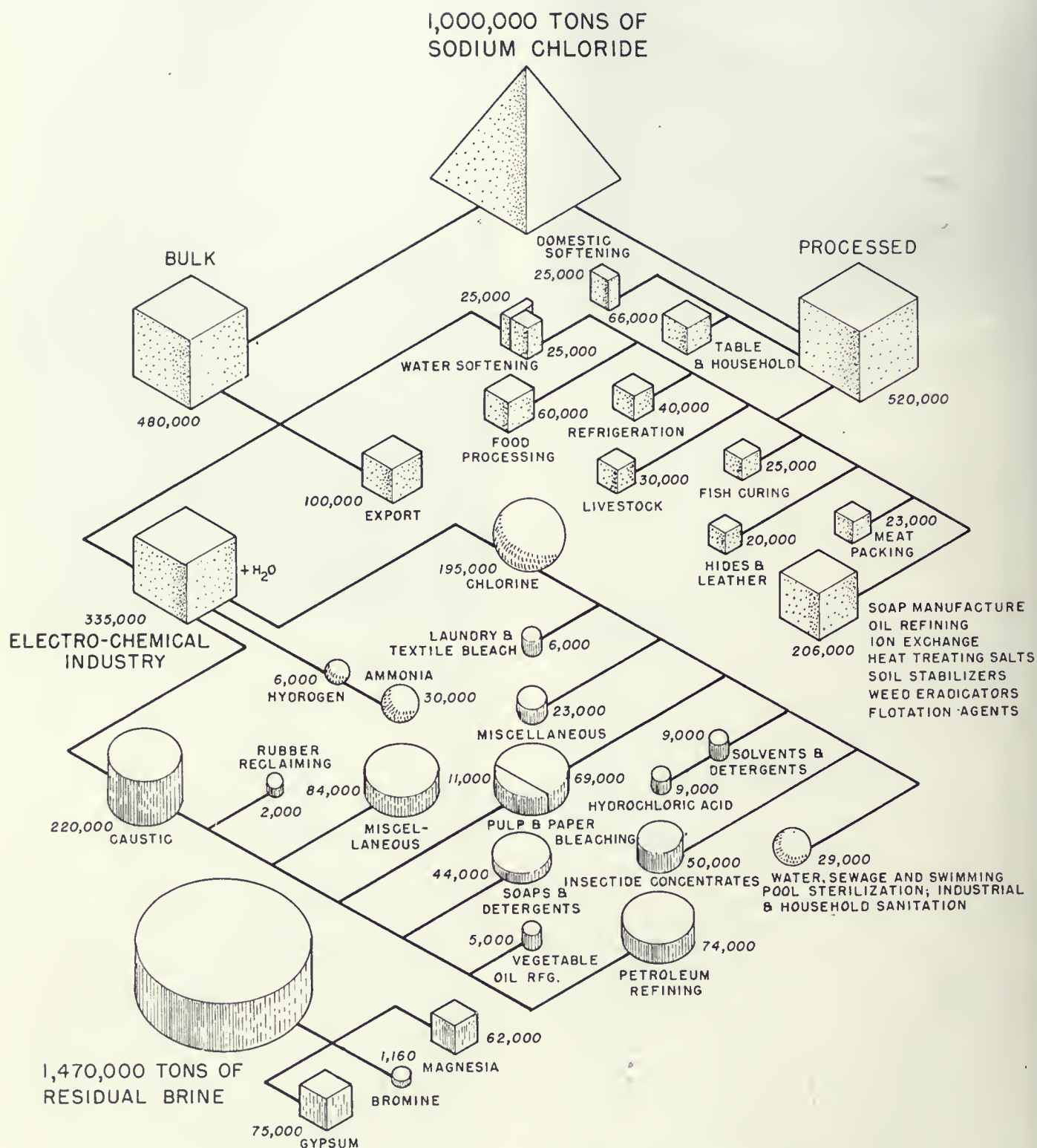
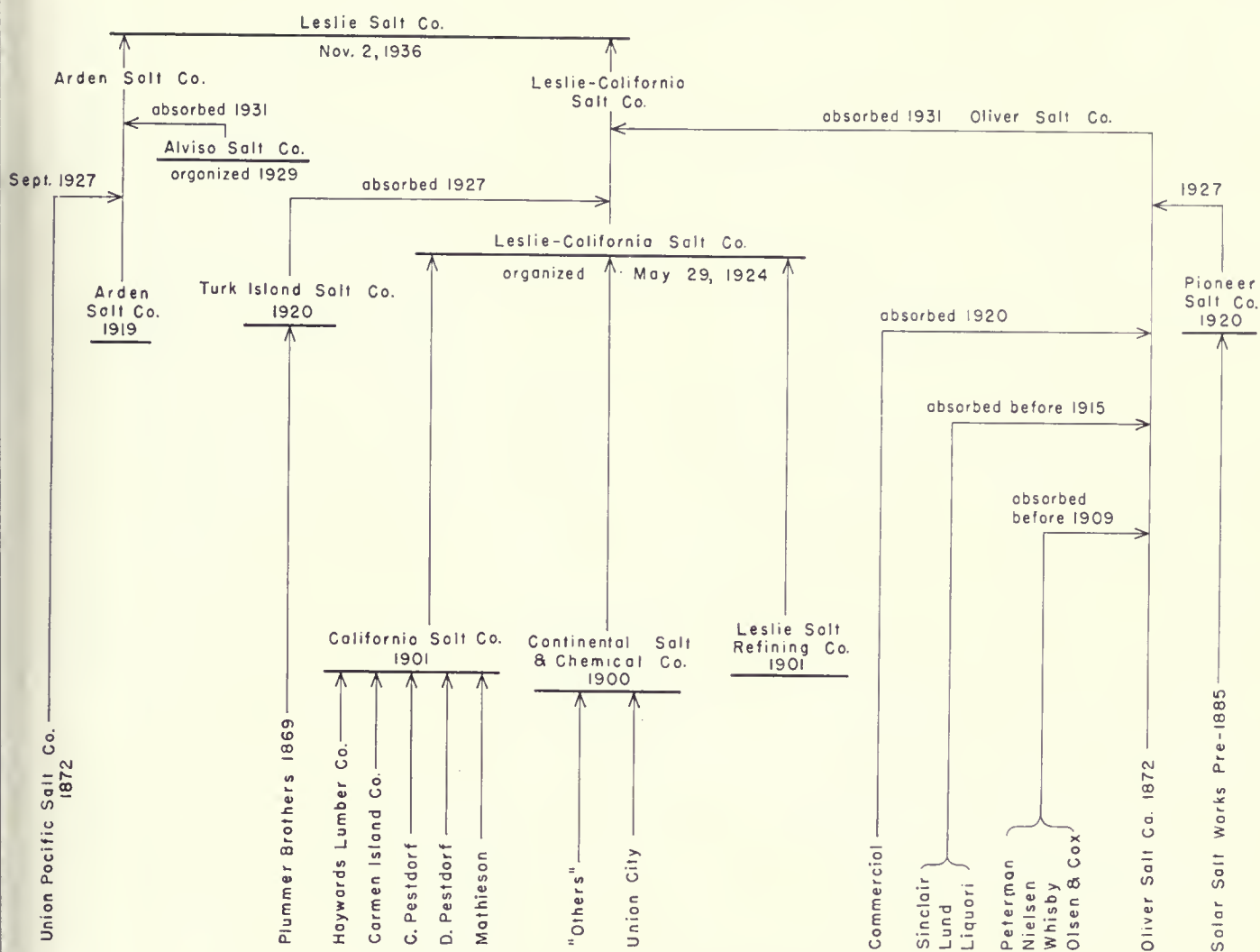


FIGURE 12. Chart showing the uses of salt produced on San Francisco Bay.





ado area and near Hayward Landing. The Continental Salt and Chemical Company built a plant near Alvarado that included existing plants as well as new land. The Leslie Salt Refining Company operation was near San Mateo. Salt was first produced in San Mateo County in 1900, and only three or four companies have operated here.

The California Salt Company, the Continental Salt and Chemical Company, and the Leslie Salt Refining Company merged to form the Leslie-California Salt Company on May 29, 1924. As part of a continuing program of increasing efficiency by modernization and expansion, two contiguous salt plants were acquired in 1927. One of these was the Oliver Salt Company, founded in 1872 and one of the largest of the 19th century salt producers. The Leslie-California Salt Company was now able to consolidate its scattered operations. The isolated San Mateo and Hayward Landing plants were closed; and the units around Alvarado were combined into two plants, the Baumberg plant north of Coyote Hills Slough, and the Alvarado plant south of it. These two plants included the greater part of the land occupied by the 19th century plants.

While these events were taking place, A. Schilling and Company organized the Arden Salt Company which produced its first crop of salt in 1919. The first comparatively small plant was at Dumbarton Point west of Newark. The Arden Salt Company grew rapidly. The first plant was expanded about 1923, and a second plant south of Newark was brought into production in 1928. Late in 1927 the Union Pacific Salt Company was purchased, but the Arden Salt Company did not operate it after 1929. The Alviso Salt Company, which owned a large area in Santa Clara County, was purchased in 1931. By 1935 the Arden Salt Company's output approximated the combined production of all the other salt companies in California.

On November 2, 1936, the Leslie Salt Co. was incorporated and took over the assets of the Leslie-California Salt Company and the Arden Salt Company. All the early producers have gone out of business or have been absorbed with the exception of the American Salt Company. A third producer, Oliver Brothers Salt Company, was founded in 1937 by younger members of the family that had owned the old Oliver Salt Company.



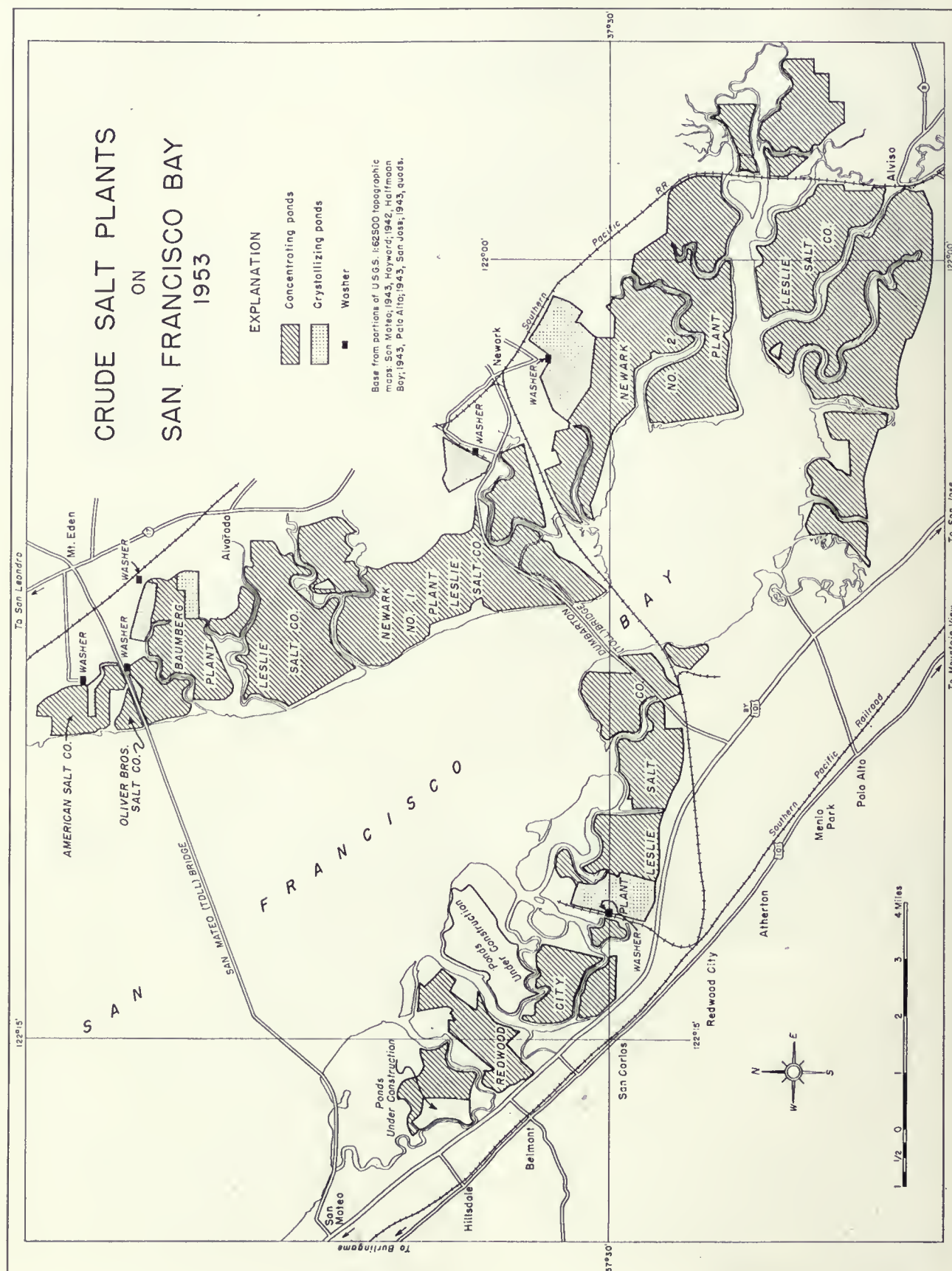


FIGURE 14. Map of the southern part of San Francisco Bay showing the locations of crude salt plants.



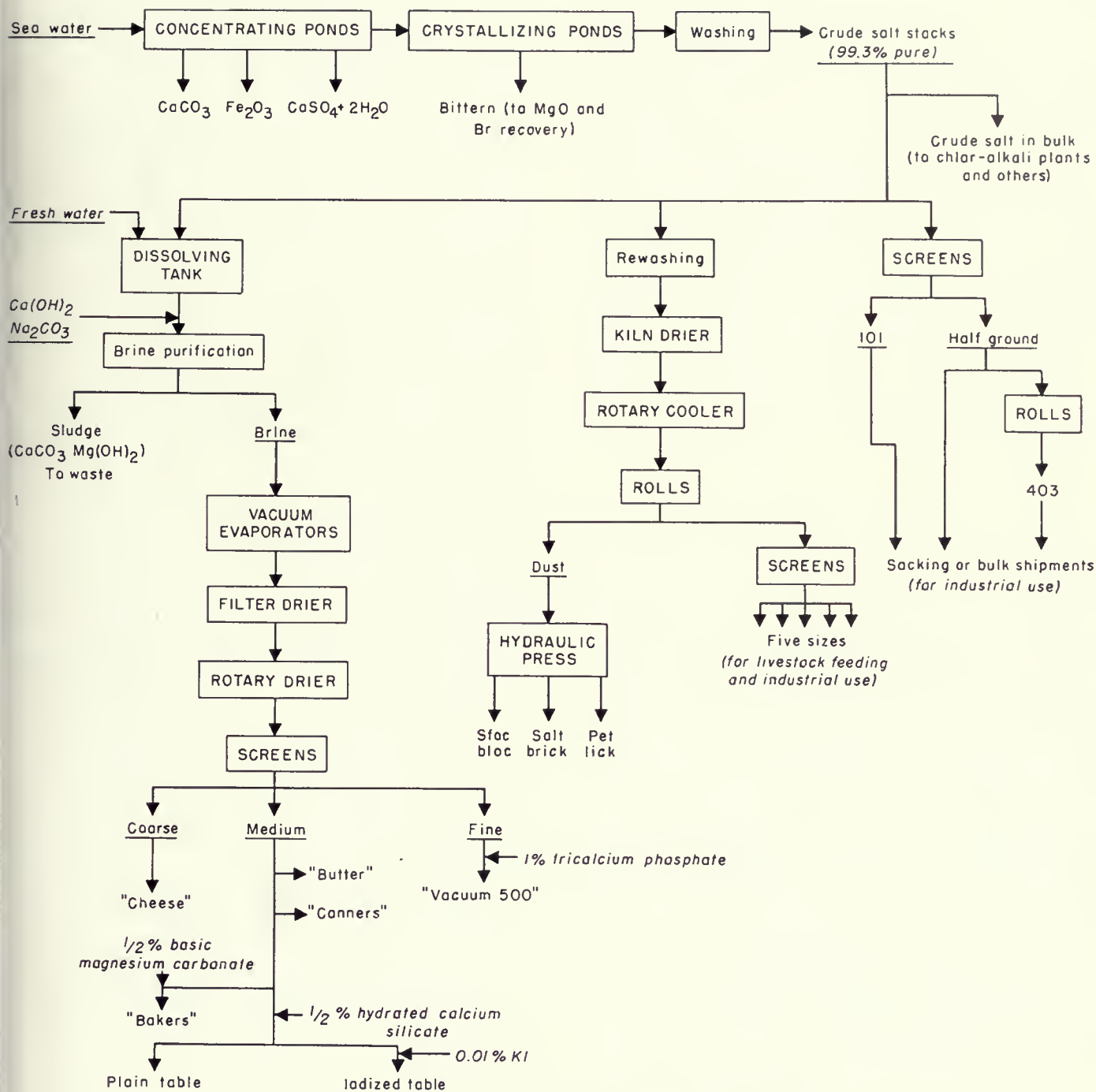


FIGURE 15. Chart showing the making of salt from sea water.



Concurrent with this consolidation has been a steady evolution in salt-making technique. Windmill-driven pumps have been displaced by gasoline and electric pumps only within the past 25 years. The revolving pick loading machine was developed in 1919 by the Continental Salt and Chemical Company and perfected by the Arden Salt Company in the 1930s. Gasoline locomotives for hauling salt cars were introduced before World War I. The Oliver Salt Company initiated the washing of salt in the 1890s, and by 1914 washing was practiced at all the larger plants. Vacuum refining was introduced in 1910.

The salt deposits of the desert region were known at an early date but were little used. The Saline Valley deposit was discovered in 1864. In the late 1880s some salt for the silver mines at Calico was mined at Danby Lake and hauled 25 miles to the railroad at Danby in wagons drawn by steam traction engines. Operations at Bristol Lake can be traced back to the Crystal Salt Company which reported a small production of salt in 1909. Salt mining at Salton Sea began in 1884 and continued until the flood of 1905 and 1906. The salt crust, 10 to 20 inches thick, was gathered into piles with plows. Salt was first produced by evaporating the water of Salton Sea about 1929.

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## SAND AND GRAVEL

(See also Specialty Sands)

By THOMAS E. GAY, JR.

In 1953, the most recent year for which statistics are available, California yielded 58,429,528 short tons of sand and gravel valued at \$53,224,203 and was the leading state in the production of these materials (Otis and Shupp 1956, p. 3). California's output in 1953 was about 14½ percent of the national total, and nearly twice that of any other state.

A marked increase in this output has occurred since World War II and is mainly attributable to increased industrial and building activity including large highway and water control projects. Approximately nine-tenths of the state's sand and gravel output is used as aggregate, in construction and road building. The remainder is mostly special sand, such as that used in glass manufacture and foundry molds (see section on special sand in this volume). Most sand and gravel aggregate is used in portland cement and macadam. Crushed stone is preferred to sand and gravel for use with bituminous binder so is used predominantly for that purpose. Oversize cobbles from sand and gravel deposits are crushed, and used mainly for bituminous-bound aggregate. Crushed stone from sand and gravel operations and from bedrock quarries is discussed in the section on crushed and broken stone.

### TERMINOLOGY AND GENERAL CHARACTERISTICS

In commercial usage, the term "sand" applies to rock or mineral fragments of natural origin, that range in diameter from 200-mesh\* to a quarter of an inch. The term "gravel" refers to naturally fragmented, commonly somewhat rounded, rock or mineral fragments that range in diameter from a quarter of an inch to 3½ inches. Silt and clay consist of grains smaller than 200 mesh. Fragments larger than 3½ inches in diameter are called cobbles and boulders.

*Mesh number and corresponding size of sieve opening, in millimeters and inches, for some commonly used sieve sizes.\**

Mesh**	Opening	
	Mm.	Inches
5	4.00	0.157
10	2.00	0.079
14	1.41	0.055
18	1.00	0.039
30	0.59	0.023
40	0.42	0.016
60	0.250	0.010
00	0.149	0.006
20	0.125	0.005
00	0.074	0.003
30	0.062	0.0026
25	0.044	0.002

\* American Society for Testing Materials specs. E 11-39, in A.S.T.M. Standards, vol. 3, p. 1544.

\*\* Number of square openings per linear inch of screen not counting thickness of wires.

Particles of sand generally consist of single minerals, whereas gravel and larger sized particles commonly con-

The term "mesh" expresses the coarseness or fineness of screens as the number of openings per linear inch: e.g. a linear inch of a 200-mesh screen contains 200 openings, each about .003 in. wide.

sist of rock comprised of several minerals. Most sand deposits of commercial importance are composed of quartz and feldspar grains, and contain minor percentages of ferromagnesian minerals and clay particles. Sand that contains a maximum of quartz grains and a minimum of clay and ferromagnesian minerals is preferred for most purposes. Quartz-rich sands, commonly known as silica sands, are desired because quartz is hard, has a high melting temperature, is chemically inert, has a high resistance to physical wear, and has a white color.

The usefulness of gravel is determined largely by the characteristics of its contained rock types, especially hardness, and resistance to chemical attack and physical wear. The value of a sand and gravel deposit for a particular use must be determined in the light of such specific factors as tonnage available, accessibility and distance to market, expense of removal of overburden as well as the physical characteristics of the material.

*Size grades of clastic fragments, in millimeters and inches.\**

Grade limit (diameter)		Name of size grade
Mm.	Inches	
*More than 256	More than 10	Boulder
*256-64	10-2½	Cobble
*64-4	2½-0.16	Pebble
*4-2	.16-.08	Granule
2-1	.08-.04	Gravel
1-.5	.04-.02	Course sand
.5-.25	.02-.01	Medium sand
.25-.125	.01-.0049	Fine sand
.125-.062	.0049-.0025	Very fine sand
.062-.004	.0025-.0002	Silt
Less than .004	Less than .0002	Clay

\* Classification according to Wentworth, after Krumbein and Pettijohn 1938, table 6, p. 80.

For ordinary sand and gravel, such as that used for aggregate, or fill, the closest deposits are sought; in contrast, some of the pure quartz sand required for specialty uses such as glass manufacture is transported for hundreds or even thousands of miles. The high cost of transporting silica sands to some areas has permitted the beneficiation of material from deposits of lower grade that occur closer to the market.

### GEOLOGICAL OCCURRENCE IN CALIFORNIA

In California, sand and gravel is obtained principally from Quaternary alluvial deposits in stream channels, flood plains, terraces, and alluvial fans. Smaller though significant quantities are obtained from Recent beach and dune sands, and from older sedimentary beds. Some deposits consist almost entirely either of sand or of gravel, but ordinarily the two occur mixed in the same deposits. The deposits in California show a wide range in size, depth of overburden and depth of water table, as well as in the physical and chemical characteristics of the material.

Crushed stone from quarries in bedrock or "ledge rock" is used for many of the same purposes as sand and gravel. Crushed ledge rock is practically indistin-



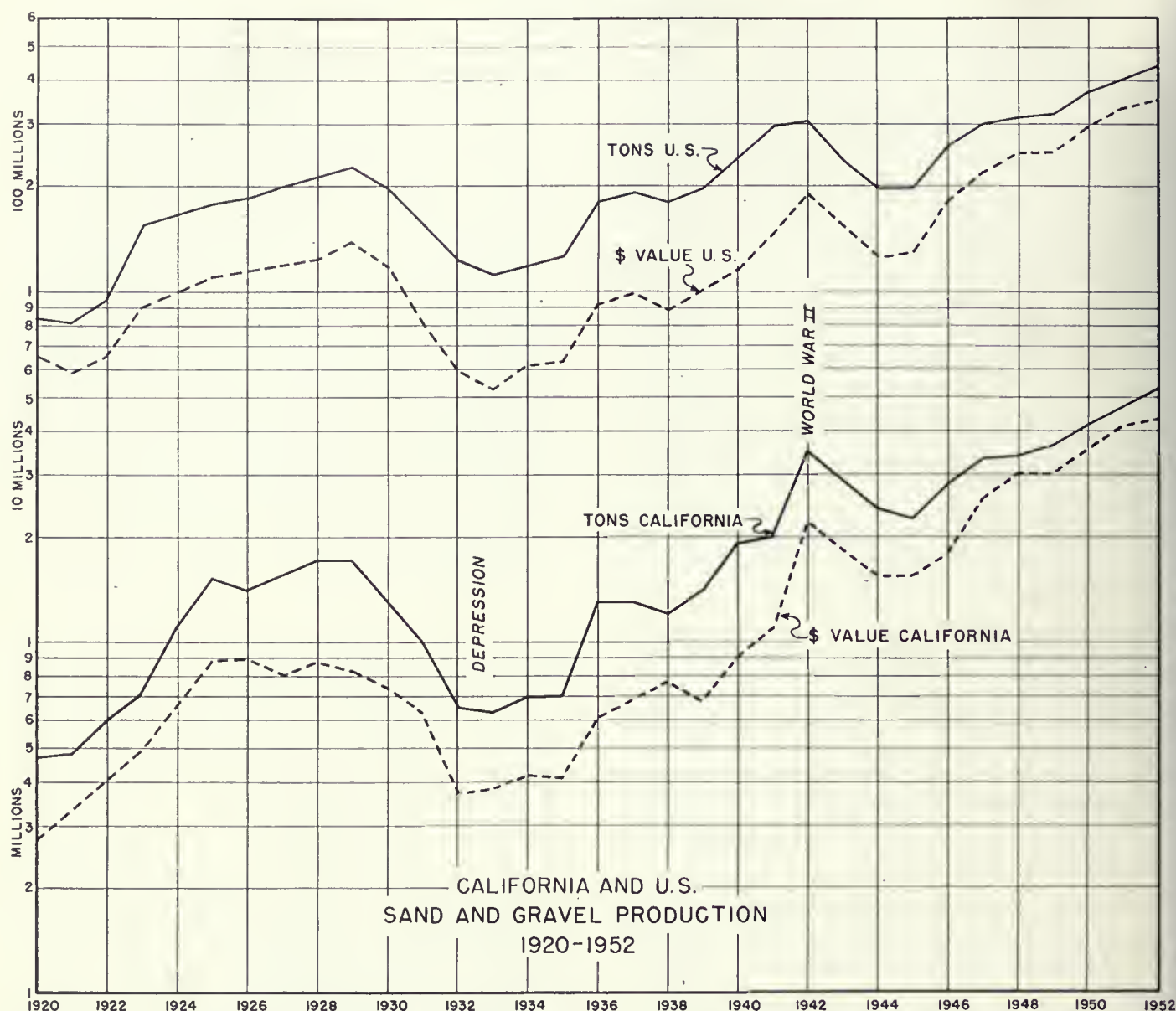


FIGURE 1. Amount (short tons), and dollar value of sand and gravel produced in California and the United States, 1920-52. After Turner, 1950, fig. 1, p. 256; U. S. Bur. Mines Minerals Yearbook and Market Repts.

guishable from crushed stone obtained by crushing cobbles and boulders from sand and gravel deposits. Crushed stone, whether produced from bedrock or from alluvial rock, is discussed mainly in the section on crushed and broken stone, in this volume.

**Stream Deposits.** In California, most stream deposits are poorly sorted, crudely stratified mixtures of sand and gravel with subordinate proportions of coarser or finer-grained material. Particle sizes range widely within the size limits of sand or gravel; the mineral grains and rock fragments commonly are sub-angular and occasionally well-rounded. Stream channel deposits in some areas are replenished by the addition of alluvium during the rainy season, so that the decrease in reserves is slight. In other areas, where urbanization has restricted the land open to sand and gravel development, the reserve problems are serious. In thick stream deposits

the deeper material is commonly less desirable than that near the surface, because it is older and more decomposed by weathering.

Usable stream-laid sand and gravel deposits underlie large areas of the state and constitute a virtually inexhaustible reserve. Under present economic conditions, however, only the deposits nearest to centers of consumption and most economical to operate are of commercial value.

**Beach and Dune Deposits.** Although beach sand and near-shore dune sand deposits yield only about 2 percent of the total sand and gravel output in California, they provide most of the special sands produced in the state. Beach and dune deposits consist mostly of sand and commonly are much more uniform in composition and are better sorted than stream deposits. Gravel and clay ordinarily are sparse or absent.



Beach and dune sands derived from granitic rocks and notably rich in quartz occur at several places along the California coast south of San Francisco. Much of the beach and dune sand along the northern California coast is derived largely from basic igneous rocks and from sedimentary rocks rich in ferromagnesian minerals, hence contains abundant dark particles and is less desirable for most purposes than quartz-rich sand.

Certain beach deposits, in both northern and southern California, are rich in the heavy minerals magnetite ( $\text{Fe}_3\text{O}_4$ ), ilmenite ( $\text{FeTiO}_3$ ), and chromite ( $\text{FeCr}_2\text{O}_4$ ) and are discussed in this volume under the heading of Black Sands.

**Tertiary Sand Deposits.** The materials obtained from partly consolidated sedimentary rocks of Tertiary age ordinarily contain a larger silt and clay fraction than stream, beach, or dune deposits. Most of the usable Tertiary deposits are farther removed from centers of consumption than Quaternary alluvial deposits. They constitute a large reserve of well-sorted sand of uniform composition, and include most of the known deposits of high-silica sands in California.

#### UTILIZATION

The material obtained from stream deposits in California is used mostly as aggregate. Most of the sand from the Recent beach and dune deposits and from Tertiary deposits is marketed for special purposes. Some of the sand that is acceptable for special uses also is used as aggregate. Material from some deposits is processed in one of several ways, depending on the intended use.

The following uses of sand and gravel are discussed below:

##### Aggregate

Portland cement concrete, including stucco, soil cement, and cement-treated road base.

Interior plaster

Bituminous-bound (asphalt) concrete, including bituminous macadam

Railroad ballast

Fill

(A wide variety of specialty uses of sand and gravel are discussed in the section on specialty sands in this volume.)

#### AGGREGATE

Aggregate is commonly defined as a hard, inert material composed of fragments which show a wide and gradational range in sizes, and which can be bound together into a coherent mass by means of a cementing material such as portland cement, gypsum plaster, or asphalt. The term also has been applied to any mass of like mineral fragments, used with or without binder

*Size grading of aggregate for plant-mixed cement-treated road base. (California Div. Highways 1949, p. 110).*

Sieve size	Percentage passing
1-inch.....	100
$\frac{3}{4}$ -inch.....	90-100
No. 4.....	40- 75
No. 30.....	15- 40
No. 200.....	3- 15

in a wide variety of ways, including uses that involve physical and chemical alteration of the aggregate material (Kriege, 1948, p. 205).

In 1953, a total of 31,711,120 short tons of sand and gravel, valued at \$28,392,638, were produced in California for use in the building industry. The 1953 output of sand and gravel used as paving material was 24,512,561 tons, valued at \$20,370,263 (Otis and Shupp, 1956, pp. 4, 5, 7). Together these two industries consumed more than 96 percent of California's output of sand and gravel. The building industry used aggregate in portland cement concrete and gypsum plaster, whereas the paving industry consumed aggregate in portland cement concrete and in bituminous concrete.

**Portland Cement Concrete Aggregate.** Portland cement concrete consists of coarse to fine aggregate surrounded and held together by hardened portland cement paste (see discussion of portland cement in this volume). Powdered portland cement is mixed with aggregate and water to form a plastic mass that can be formed into various shapes. Chemical action between the cement and water causes complex hydrous calcium aluminum silicates to crystallize and bind the mass into a hard monolithic unit. Concrete mixes commonly contain 15 to 20 percent water, 7 to 14 percent cement, and 66 to 78 percent aggregate.

The quality of the concrete is a major factor in determining the quality of the concrete. Aggregate specifications for various uses have been established by several agencies such as U. S. Bureau of Reclamation, U. S. Army Corps of Engineers, and California Division of Highways, to insure that aggregate is satisfactory for particular types of use. These agencies and other major consumers of concrete test aggregate for acceptance by standard test procedures outlined by such organizations as the American Society for Testing Materials, and the American Association of State Highway Officials. These specifications have been subject to minor variations which reflect slight differences in usage procedures or in engineering opinion, or have been necessary to permit use of available local materials for economic reasons.

Portland cement concrete aggregate should be clean, hard, sound, durable, and of uniform quality. It should be free of soft, friable, thin, or laminated fragments, organic matter, oil, alkali, or other deleterious substances. Specific gravity, color, lack of chemically reactive ingredients, compressive strength, and roundness of particles are important in some uses.

Most aggregate specifications have been established to insure strong, sound concrete that will withstand the physical and chemical effects of weather and use. Color is important mainly in sand used for stucco or plaster finishes. Round or equant particles are desired to improve workability of cement as it is poured. If angular, flat, or elongated particles exceed about 15 percent of the volume of the aggregate, workability may be maintained by increasing the proportions of sand and water, which reduces the strength, or by increasing the proportion of cement, which in turn raises the cost.

Certain mineral substances, such as gypsum, zeolite, pyrite, opal, chalcedony, chert, siliceous shale, volcanic glass, and some acid volcanic rocks, are undesirable in aggregate. Gypsum shortens the setting time of cement;



*Numerical list of sand and gravel operations active in 1953.**(For locations see accompanying map, figure 2.)***Alameda County**

1. Bell Sand and Gravel Co.
4. Henry J. Kaiser Co., Niles
5. Henry J. Kaiser Co., Radium
7. Pacific Coast Aggregates, Centerville
8. Pacific Coast Aggregates, Elliot
9. Pacific Coast Aggregates, Niles
10. Rhodes and Jamieson Ltd.
- 12A. California Rock and Gravel Co.

**Butte County**

12. Butte Creek Rock Co.
13. Gene Holland
14. Henry J. Kaiser Co.
15. Marler Rock Co.
16. Mathews Ready Mix

**Calaveras County**

17. Nelsen Sand and Gravel Co.

**Colusa County**

18. Cortina Sand, Gravel, and Silt Co.
19. Paul Entremoot

**Del Norte County**

26. Crescent City Rock Co.
27. Peters Rock Co.
29. Simpson Logging Co.
30. Marin Tryon

**El Dorado County**

31. El Dorado Rock and Sand Co.

**Fresno County**

32. Anderson Rock Supply
33. Atchison, Topeka, and Santa Fe Railway Co.
34. Central Rock and Sand Co.
35. L. D. Folsom, Inc.
36. Herndon Rock Products Co.
37. Pacific Coast Aggregates
38. Gene Richards
39. Sanger Rock and Sand
42. Thompson Materials Co.

**Glenn County**

43. L. G. Madsen and L. J. Paul
44. Orland Sand and Gravel Co.
45. W. J. Rabbitt Co.
46. Southern Pacific Co.

**Humboldt County**

47. Eureka Sand and Gravel Co.
49. Mad River Sand and Gravel Co.
50. McWhorter and Dougherty

**Imperial County**

51. Valley Transit Cement Co.

**Kern County**

53. C and H Materials Co.
54. Griffith Co.
55. Hartman Concrete Materials Co.
56. Kern Rock Co.

**Lake County**

57. F. M. Frazell Co.
58. Lange Bros.

**Lassen County**

59. Grayson Concrete and Materials

**Los Angeles County**

6. (San Fernando Valley producing district:)
  - Arrow Rock Co., Sun Valley
  - Blue Diamond Corp., Sun Valley
  - California Materials Co.
  - City Rock Co.
  - Consolidated Rock Products, Roscoe
  - Consolidated Rock Products, Hewitt
  - Granite Materials Co.
7. (San Gabriel Valley producing district:)
  - Arrow Rock Co., Duarte
  - Azusa Rock and Sand Co.
  - Blue Diamond Corp., Santa Fe
  - Century Rock Products
  - Consolidated Rock Products Co., Irwindale
  - Consolidated Rock Products Co., Largo
  - Consolidated Rock Products Co., Sierra
  - Graham Bros., Inc.

Livingston Rock and Gravel Co.  
Manning Brothers Rock and Sand Co.

- Osborn Co.
- Owl Rock Products Co.
- Pacific Rock and Gravel Co.
- Sierra Rock Products Co.
- Sparks and Mundo Engineering Co. (Palos Verdes area:)
- Chandler's Palos Verdes Sand and Gravel
- Sidebotham and Son, Inc.
- Torrance Sand and Gravel Co.
85. MacArthur and Son

**Madera County**

97. Thompson Materials and Construction Co.

**Mariposa County**

101. G. P., J. G., and E. C. Greenauger Co.

**Merced County**

102. William J. Saye
103. Ford Gravel Co.
104. Ukiah Gravel and Cement Co.

**Merced County**

105. Cressey Sand and Gravel Co.
106. Le Grand Sand and Gravel Co.
107. Los Banos Gravel Co.
108. River Rock Co.
109. Turlock Rock Co.
110. Valley Aggregates

**Monterey County**

115. M. J. Murphy

**Napa County**

120. Benson Gravel Plant

**Nevada County**

121. Greenhorn Sand and Gravel Co.
122. Bob Winkle

**Orange County**

8. (Santa Ana-Orange producing district:)
  - Burris Sand Pit
  - California Rock Co.
  - Consolidated Rock Products Co.
  - Foster Sand and Gravel Co.
  - A. E. Fowler and Sons
  - Graham Bros. Inc.
  - McClellan and Sons
  - P. J. Noble
  - Orange County Rock Products Co.
  - Sully-Miller Construction Co.

**Placer County**

136. Joe Chevreux, Contractor

**Riverside County**

140. Desert Rock Co.
142. Massey Rock and Sand Co.
145. Palm Springs Builders Supply Co.
146. San Geronio Rock Products Co.

**Sacramento County**

2. (Sacramento producing district:)
  - Asta Construction Co.
  - American River Sand and Gravel Co.
  - Brighton Sand and Gravel Co.
  - Del Paso Rock Co.
  - Fair Oaks Sand and Gravel Co.
  - Haggin Gravel Co.
  - Hard Materials Co.
  - McGillivray Construction Co.
  - Pacific Coast Aggregates
  - Perkins Gravel Co.
  - Robert Powell Co.
  - Robertson's Sand and Gravel Co.

**San Bernardino County**

9. (San Bernardino producing district:)
  - Fontana Gravel Co.
  - Fourth Street Rock Crusher
  - George Herz and Co.
  - Holiday Rock Products Co., Colton
  - Holiday Rock Products Co., Upland
  - Service Rock Co.
  - Triangle Rock and Gravel Co.
  - Tri-City Rock Co.
- (Claremont area:)
  - Consolidated Rock Products Co.
  - Hanawalts
  - Edwin C. Hill

**San Diego County**

177. Canyon Rock Co.
178. Caudell and Johnson, Mission Valley
179. Caudell and Johnson, Poway Valley
181. Daley Corp.
182. Denton's Sand Plant
184. Escondido Sand and Gravel Co.
185. Fenton Material Co., Murray Canyon
186. Fenton Material Co., Mission Valley
187. Fenton Material Co., Otay
190. Monarch Materials Co.
191. Nelson and Sloss
192. Carl Niemann
193. Rohl Co., Inc.

**San Joaquin County**

197. Pacific Coast Aggregates Co.
198. Putnam Sand and Gravel Co.
199. Tracy Rock and Gravel Co.
200. Claude C. Wood Co.
- 200A. Neil Ellsbury

**San Luis Obispo County**

202. Walter B. Rosellip

**Santa Barbara County**

207. Buell Flat Rock Co.
208. Southern Pacific Milling Co.
209. Valley Sand and Gravel Co.

**Santa Clara County**

210. J. C. Bateman
211. Los Gatos Construction Co.
212. Los Gatos Sand and Gravel Co.
214. Leo F. Piazza Paving Co.
215. Ralsch Paving Co.
218. Western Gravel Corp.
219. Western Tile and Supply Co.

**Santa Cruz County**

220. Hansen, Silvey, and Sinnott
222. V. W. Maddock
223. Pacific Coast Aggregates Co.
224. Santa Cruz Aggregate Co.

**Shasta County**

225. Frederickson and Watson
226. J. H. Hein
227. Oaks Sand, Gravel and Cement Co.
228. Bert C. Peeler

**Siskiyou County**

229. J. S. Jensen and M. N. Thompson

**Sonoma County**

234. Basalt Rock Co.
238. Marshall Maxwell
240. L. T. Willig

**Stanislaus County**

241. American Sand and Gravel Co.
244. Frank B. Marks, Jr.
245. Modesto Sand and Gravel Co.
247. Santa Fe Rock and Sand Co.
248. Standard Rock Co.
249. Charles D. Warner and Son

**Tehama County**

251. Allen, Holseman, and Paulsen
252. Frederickson and Watson

**Trinity County**

253. Trinity Sand and Gravel Co.

**Tulare County**

254. Middleton-Sequela Co.
255. Pacific Coast Aggregates, Lemon Cove
256. Pacific Coast Aggregates, Lindsay

**Tuolumne County**

257. Beerman and Jones

**Ventura County**

259. Montalvo Rock Co.
260. Saticoy Rock Co.
261. Southern Pacific Milling Co.

**Yolo County**

262. Madison Sand and Gravel Co.
263. Pacific Coast Aggregates Co.
264. Perkins Gravel Co.
265. W. C. Railing
266. Schwarzgruber and Sons



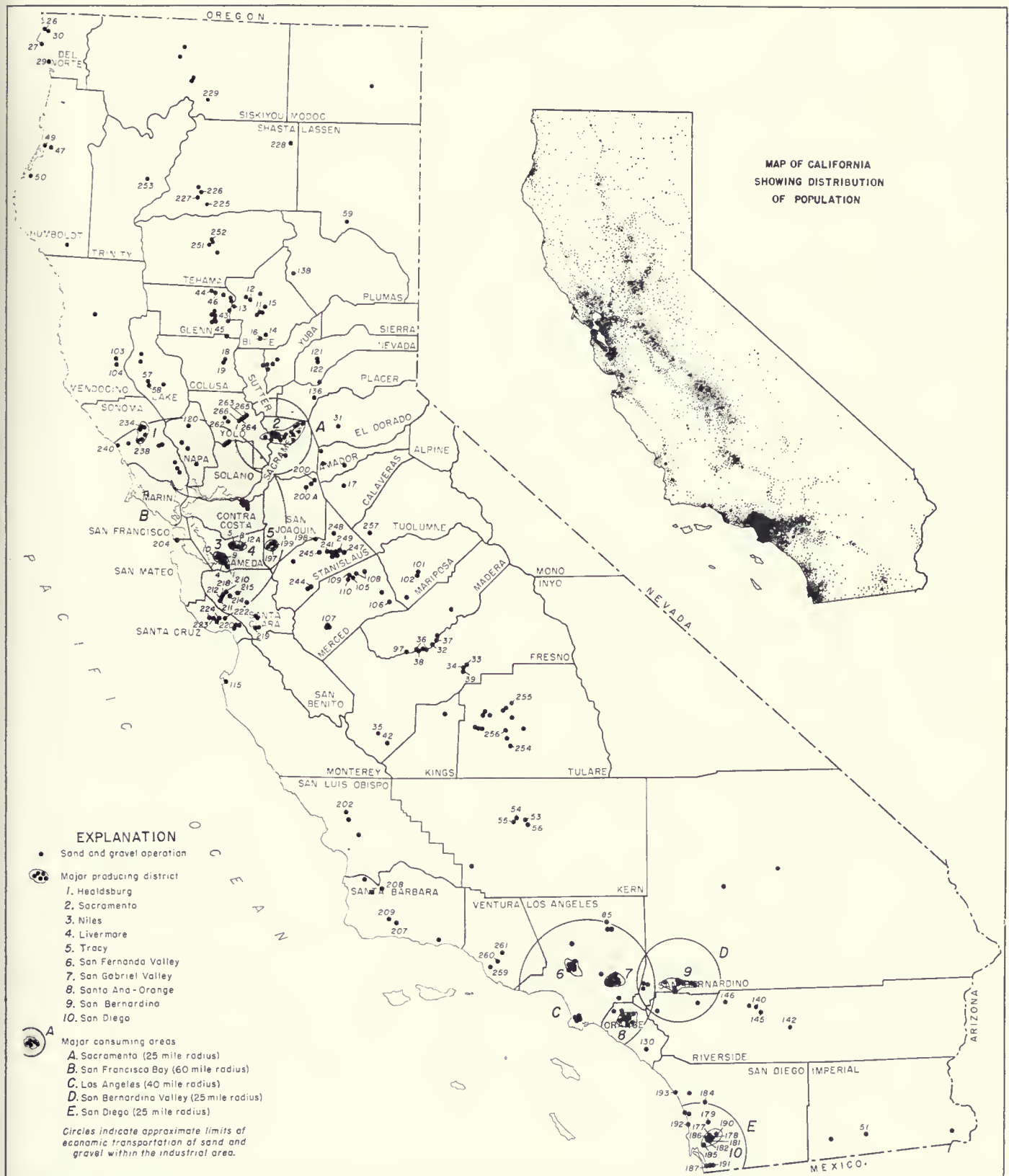


FIGURE 2. Map showing locations of the most productive sand and gravel operations in California. Most of these have been active since 1950. Ten major producing districts and five major consuming areas are indicated. From U. S. Bur. Mines and California Div. Mines records.



*Quality of concrete aggregate.*

Property of aggregate	Importance in concrete	Test methods	Reference to tests
Cleanness (lack of dirt, clay, or silt finer than 200 mesh)	Determines quality of bond with cement.	Measure material passing 200-mesh sieve; measure suspended material after shaking in water.	ASTM test C117-49 (ASTM 1954, pp. 47-48)
Hardness and durability (resistance to abrasion)	Affects strength, resistance to wear.	"Los Angeles Rattler"; measure proportion of fine material produced by abrasion in revolving metal drum after 100 and 500 turns.	ASTM test C131-51 (ASTM 1954, pp. 40-42)
Toughness	Affects strength, resistance to wear.	Impact; measure distance a standard-size hammer drops on specimen to fracture it.	ASTM test D3-18 (ASTM 1951, pp. 88-89)
Soundness (lack of fissures in particles)	Affects strength, susceptibility to frost damage from expansion of absorbed water.	Alternately soak in sodium or magnesium sulfate solution and dry; crystallization of absorbed solution forces open invisible cracks.	ASTM test C88-46T (ASTM 1954, pp. 76-81)
Lack of soft or friable fragments	Affects strength, resistance to wear.	Scratch test using brass rod of Rockwell hardness B65 to B75; rock softer than rod is unsatisfactory.	ASTM test C235-54 (ASTM 1954, pp. 74-75)
Lack of organic matter (coal, lignite, organic impurities)	Affects strength, resistance to wear.	Separate material lighter than 2.0 specific gravity in heavy liquid, and weigh; compare color of sample with standard color solution—dark color assumed due to organic material.	ASTM tests C123-53T and C40-48. (ASTM 1954, pp. 51-52; 56).
Unit weight	Determines mass.	Weigh aggregate contained in standard cubic foot measure.	ASTM test C29-42 (ASTM 1954, pp. 90-91)
Specific gravity—dry and with absorbed liquid	Determines mass (specific gravity commonly specified 2.5 or more); absorption affects bond of cement paste to particles.	Compare oven-dry weight with immersed weight, and weight after surface re-dried.	ASTM tests C127-42, and C128-42 (ASTM 1954, pp. 82-83; 84-85)
General characteristics: 1. Particle shape 2. Character of surface 3. Grain size 4. Texture (e.g. pore-space, grain packing, cementation) 5. Color 6. Mineral composition 7. General physical condition (e.g. weathering) 8. Presence of potentially deleterious chemical substances (e.g. gypsum, zeolite, pyrite, opal, chalcedony, volcanic glass)	Different effects on strength, hardness, color, and permanence of concrete.	Examine by naked eye, hand lens, and under petrographic microscope.	ASTM test C295-54 (ASTM 1954, pp. 97-106)
Potential chemical reactivity	Affects permanence of concrete; reactive substances cause "pop-outs" and failures due to expansion.	Weigh silica dissolved in sodium hydroxide solution; measure reduction in alkalinity caused by immersion of sample in standard sodium hydroxide solution.	ASTM test C289-54T (ASTM 1954, pp. 54-63)
		Measure expansion under controlled conditions, in sample bar of mortar made with aggregate in question.	ASTM test C227-52T (ASTM 1954, pp. 296-303)
Size grading characteristics	Affects flowability, residual void spaces, strength.	Standard sieve analysis: screen in standard-size screens; weigh various fractions; plot on appropriate graphs.	ASTM test C136-46 (ASTM 1954, pp. 69-71)
Sand Equivalent (California only)	Affects permanence of concrete.	Determine relative proportions of detrimental fine dust or claylike materials present, by elutriation processes.	Div. of Highways Mat. & Research Dept. Method No. Calif. 217-A

*Grading requirements of several commonly used sizes of aggregate, showing required percentage distribution of fragments within the maximum and minimum size limits. Gradings designated "combined aggregate" are prepared by combining the primary gradings (California Div. Highways, 1954, p. 181).*

Sieve size	Weight percentage passing sieve							
	Primary aggregate					Combined aggregate		
	2½" to 1½"	1½" to ¾"	1" to No. 4	¾" to No. 4	Fine	2½" max.	1½" max.	¾" max.
3"-----	100	--	--	--	--	100	--	--
2½"-----	90-100	--	--	--	--	95-100	--	--
2"-----	35-70	100	--	--	--	80-95	100	--
1½"-----	0-15	90-100	100	--	--	65-87	90-100	--
1"-----	--	20-55	90-100	100	--	50-75	50-86	100
¾"-----	0-5	0-15	60-85	90-100	--	45-66	45-75	90-100
⅝"-----	--	0-5	15-40	20-55	100	38-55	38-55	60-80
No. 4-----	--	--	0-15	0-15	90-100	30-45	30-45	40-60
No. 8-----	--	--	0-5	0-5	65-90	23-35	23-35	30-45
No. 16-----	--	--	--	--	45-70	17-27	17-27	20-35
No. 30-----	--	--	--	--	25-45	10-17	10-17	13-23
No. 50-----	--	--	--	--	10-20	4-9	4-9	5-15
No. 100-----	--	--	--	--	2-8	0-3	0-3	0-5
No. 200-----	0-2	0-2	0-2	0-2	0-4	0-2	0-2	0-2



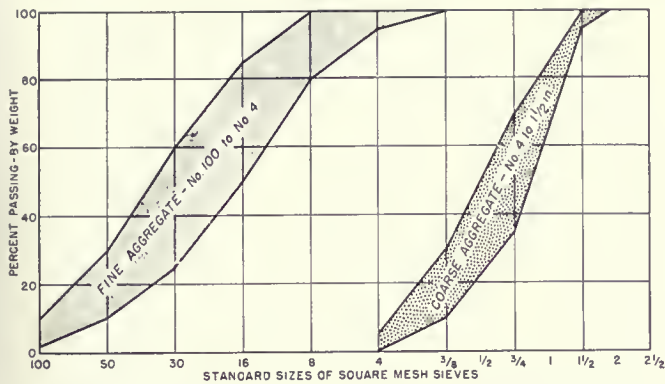


FIGURE 3. Size ranges of fine and coarse aggregate. Areas between curves indicate acceptable sizings under specification C 33-54T for fine aggregate (No. 100 to No. 4 sieves) and one size of coarse aggregate (No. 4 to 1½-inch sieves). After ASTM 1955, pp. 1, 3.

pyrite dissociates to yield sulfuric acid and iron oxide stain. The other substances noted above contain silica in a form that reacts with alkali substances in the cement.

A colloidal material, thus formed, absorbs water and increases in volume as the concrete hardens. Internal expansion may continue for as long as two years, and result in serious cracking, as well as surface pits known as "popouts." If reactive aggregate is unavoidable, alkali reactions can be controlled by addition of pozzolan to the mix or by use of low alkali cement.

Sand and gravel that meet physical requirements must be marketed in the size ranges that are specified for particular uses. A different size range is specified for concrete mixes to be used for each of the following products: pavements, curbs, walks and gutters, structural walls, piers, mortar, plaster, and stucco. Fragment size distribution within the maximum and minimum limits also is closely specified.

Aggregate is divided into two main size ranges: fine aggregate, from 200 mesh to ¼ inch; and coarse aggregate, larger than ¼ inch. The grading and maximum size of aggregate largely determine the relative proportions of ingredients to be used, as well as the workability, economy, porosity, and shrinkage of the concrete (Portland Cement Association 1952, pp. 11-13). The largest

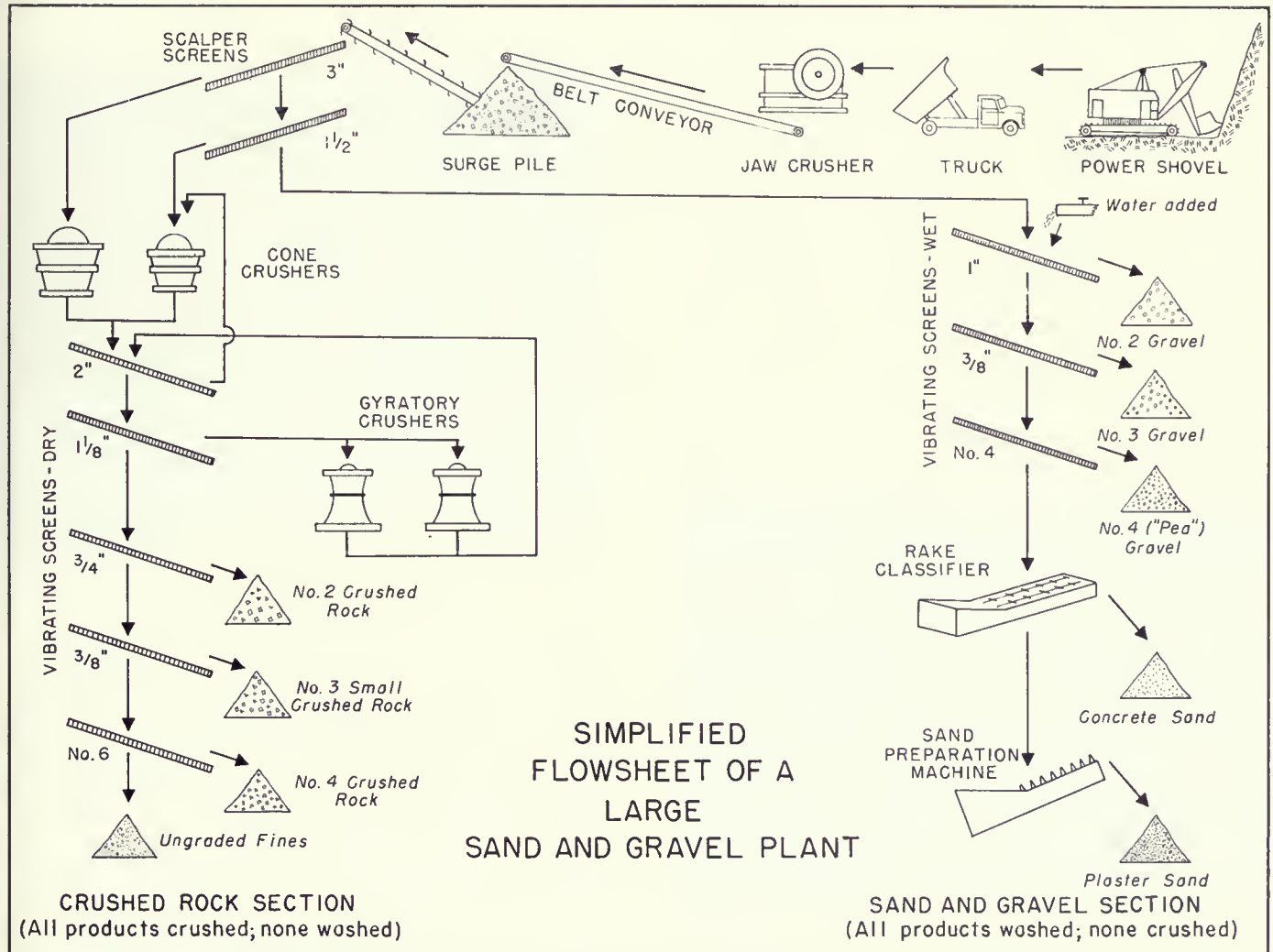


FIGURE 4. Generalized flowsheet of a typical large (200 to 1000 tons per hour) plant producing sand, gravel, and crushed stone from alluvial deposits. By varying size, number, and position of screens, and adjusting crusher settings, a variety of sand, gravel, and crushed stone can be produced. Water is added for all screening and classifying in the sand and gravel section, to wash away excess fine material.





FIGURE 5. Photo showing character of sand and gravel in river flood-plain deposit of Pleistocene Victor formation, exposed in pit of Perkins Gravel Company, Sacramento County. Layers of light and dark sand are well sorted, in part cross-bedded; pebbles are well rounded.

practicable size of coarse aggregate is desirable, but generally the maximum size should not exceed  $\frac{1}{5}$  the minimum dimension of the member nor  $\frac{3}{4}$  the clear spacing between reinforcing bars. In fine aggregate, the larger the fraction that passes the No. 50 and 100 sieves, the greater the workability; the smoother the finish and surface texture; but the greater the water gain.

Most natural deposits of sand and gravel contain too much material of sizes finer than 200 mesh, and oversize cobbles also are commonly present. Except in small local operations, therefore, pit-run material is carefully washed and screened into appropriate sizes which then commonly are blended in specified proportions.

Stucco is a special type of portland cement concrete, in which only fine aggregate—concrete and plaster sand—are used. Stucco is used on outside surfaces, whereas plaster is used only inside.

Soil cement is a rather low-grade type of portland cement concrete, formed by mixing portland cement with



FIGURE 6. Photo showing character of sand and gravel in marine deposit of Cretaceous (?) Novato conglomerate, exposed in pit of Black Point operation of Niles Sand and Gravel Company, in Marin County. There is a general lack of sorting or bedding, and a high degree of rounding of pebbles and cobbles.

*Nominal size specifications of the main classes of aggregate produced by most companies in Los Angeles County. (Gay and Hoffman, 1954, p. 559.)*

<b>Crushed rock (not washed)</b>	
No. 1 crushed rock.....	3½" to 1½"
No. 2 crushed rock.....	1½" to ¾"
No. 3 crushed rock, large.....	1" to ½"
No. 3 crushed rock, small.....	¾" to ⅜"
No. 4 crushed rock.....	⅜" to No. 6
<b>Gravel (washed)</b>	
No. 1 gravel.....	2½" to 1½"
No. 2 gravel.....	1½" to ¾"
No. 3 gravel.....	1" to ⅜"
No. 4 gravel ("pea").....	⅜" to No. 4
<b>Sand (washed)</b>	
Concrete sand.....	No. 4 to 0
Plaster sand.....	⅜" to 0

pulverized natural earthy material. The mixture is compacted and watered so the cement hardens. This practice, increasingly common in road-building in California, results in stronger, more stable subgrade to support paving courses (for details see California Div. Highways 1954, pp. 96-110). Neither sand and gravel nor crushed stone is used, as such, in soil cement and specifications for the aggregate are necessarily very lenient.

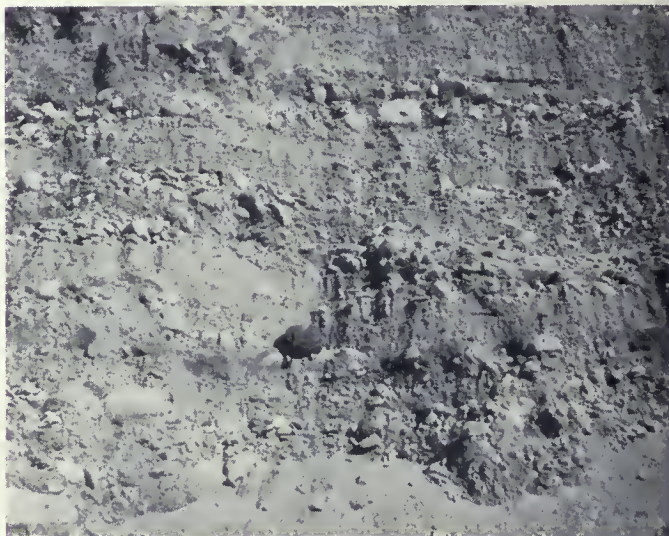


FIGURE 7. Photo showing typical poorly sorted and poorly bedded dry wash deposit, as exposed in pit of Osborn Company, Eaton Wash, Los Angeles County. Canteen is about 14 inches in diameter. Degree of rounding of larger cobbles and boulders varies.

Cement-treated road base (California Div. Highways 1954, pp. 96-108) is a type of portland cement concrete that is intermediate in quality between soil cement and normal concrete. It is used as base course to give stable support for paving courses in road construction. Road-mixed cement-treated base (California Div. Highways 1954, pp. 101-102) commonly has the natural material of the roadbed for aggregate and corresponds to soil cement. Plant-mix cement-treated base (California Div. Highways 1954, pp. 102-104) serves the same function but requires aggregate free from adobe, vegetable matter and other deleterious substances and uniformly graded.

*Interior Plaster Aggregate.* Interior plaster consists of fine-grained aggregate held together by a solidified



Size distribution in concrete sand and plaster sand.

Standard sieve sizes, square screen openings	Percentage passing*		
	A	B	C
3/4-inch-----	100		
No. 4 (4760-micron)-----	90-100	95-100	100
No. 8 (2380-micron)-----	65- 90	80- 90	95-100
No. 16 (1190-micron)-----	45- 70	60- 80	70- 95
No. 30 (590-micron)-----	25- 45	30- 60	35- 70
No. 50 (297-micron)-----	10- 20	12- 30	5- 35
No. 100 (149-micron)-----	2- 8	2- 8	0- 10

\* (A) Distribution of particle sizes within the size range of concrete sand, (Los Angeles County Road Department, 1949, Rock, gravel, sand, and stone dust: Standard specifications, section 37, p. 4). (B) Distribution of particle sizes in concrete sand, specified by U. S. Bureau of Reclamation (Portland Cement Association 1952, p. 12). (C) Sieve analysis required of sand for use in interior plaster (A.S.T.M. specification (tentative) C35-54T: ASTM 1954, p. 310).

paste of cementing material. It is used to cover walls and ceilings. In recent years more and more attention has been paid to the acoustical qualities of interior plaster. Plaster aggregate formerly consisted entirely of fine sand ("plaster sand"), but in the past decade lightweight aggregate, especially perlite, has largely replaced sand in this use (see section on pumice, in this volume).



FIGURE 8. Photo showing unconsolidated stream-bed deposit, in Cache Creek, Yolo County. Deposit is well sorted and well bedded, and fine sizes of gravel predominate.

Portland cement formerly was the binder most used in plaster, but in the past several decades gypsum cement has almost entirely replaced it in this use except where waterproof walls are required.

Gypsum cement consists of artificially prepared, nearly anhydrous calcium sulfate mixed with inert substances such as hemp fiber or wood pulp. One part of dry gypsum cement is added to about two and a half parts of aggregate, and enough water to make the mass plastic for application. Crystalline hydrous calcium sulfate (gypsum) soon forms, which binds the plaster in solid form.

Besides meeting size requirements, aggregate for plaster must have uniformly light color, less than 0.15 percent water-soluble impurities, and be free of detrimental quantities of organic impurities (A.S.T.M. tentative

specification C35-54T for inorganic aggregates for use in interior plaster: A.S.T.M. 1954, pp. 310-312). Other qualities generally required of portland cement concrete aggregate also apply to plaster aggregate.

**Aggregate Used with Bituminous Binder.** Sand and gravel or crushed stone aggregate is commonly bound together by a bituminous material such as asphalt or tar to make asphalt concrete, also known as bituminous concrete (ASTM 1954), or bituminous macadam (California Div. Highways 1949, pp. 166-186), which are used primarily as a paving material. Unlike portland cement concrete, bituminous-bound concrete and macadam are slightly plastic under very great or long-applied stresses. Sand and gravel may be used for bituminous-bound aggregate, but crushed stone is preferred because broken surfaces adhere better to the binder than do rounded ones, and the interlocking of angular particles strengthens the concrete (for more details see section on crushed and broken stone).

#### DEPOSITS IN CALIFORNIA

Recent stream deposits, including stream bed, dry wash, bank, and terrace deposits, are widely distributed in California, and yield almost all the sand and gravel aggregate produced in the state. In northwestern California, deposits along the Smith and Klamath Rivers supply the Crescent City area, Del Norte County, and deposits along the Mad and Eel Rivers supply the Eureka area, Humboldt County. In the Sacramento Valley, northern portion of the Great Valley, deposits along the Sacramento River, and its tributary creeks and rivers, provide sand and gravel aggregate for consumption at Redding, Shasta County; Red Bluff, Tehama County; Chico, Butte County; Marysville, Yuba and Sutter Counties; and Sacramento, Sacramento County. On the west side of the Sacramento Valley, stream deposits along Cache and Putah Creeks provide aggregate for the Woodland and Winters areas, Yolo County. On the east side of the Sacramento Valley, deposits are active along the Feather River, near Oroville, Butte County; the Yuba River, near Marysville; the American River, near Sacramento; and the Mokelumne River, near Clements, San Joaquin County.

In central California, deposits along the Russian River yield sand and gravel near Ukiah, Mendocino County; and Healdsburg and Petaluma, Sonoma County. The large tonnages of sand and gravel consumed in the San Francisco Bay area are obtained mainly from deep uplifted stream cone deposits of ancestral Alameda Creek, in the Niles-Centerville area, Alameda County; and from valley fill alluvium along Arroyo del Valle and Arroyo Mochio in the Livermore-Pleasanton area. Other stream deposits that supply the San Francisco Bay area market are located along Corral Hollow Creek, near Tracy, San Joaquin County; Coyote, Los Gatos, Guadalupe, and Carnadero Creeks near San Jose, Santa Clara County; and the Russian River near Healdsburg.

In the San Joaquin Valley, which is the southern portion of the Great Valley, the principal stream deposits of sand and gravel occur along the San Joaquin River and its tributaries. On the east side of the valley, active deposits occur along the Stanislaus River near Riverbank, Stanislaus County; the Tuolumne River east of Modesto, Tuolumne County; the Merced River near



*Summary of sand and gravel producers of California.*

Main producing areas <sup>1</sup>		Types of deposits	Type and source of rocks present	Commercial producers active (1953) <sup>2</sup>	Approximate total annual output (1953) <sup>2</sup> (short tons; value)	Main products <sup>4</sup>	Remarks, references <sup>5</sup>
Marketing area	Locations of deposits						
Northern California Crescent City-Eureka area. (Coastal regions of Del Norte and Humboldt Counties.)	Elk Creek; Smith, Klamath, Mad, and Eel Rivers.	Recent stream bed and river bar alluvium.	Metavolcanic, granitic and chert rocks derived from the western Klamath Mountains; graywacke and other sandstones, jasper, and quartzose rock derived from northern Coast Ranges.	7	950,000 \$900,000	Sand, gravel, and crushed cobble aggregate; mill road ballast.	Used mainly in asphaltic concrete for paving. Many operations intermittently active, according to demand. Seasonal replenishment of most stream deposits.  (Averill 1941, pp. 527-528, Humboldt Co.; O'Brien 1952B, pp. 279-280, Del Norte Co.)
Redding-Red Bluff area. (Upper Sacramento River in Shasta, Tehama, Glenn, and Colusa Counties.)	Sacramento River, tributary creek beds and dry sloughs.	Recent stream bed and dry wash alluvium.	Mainly andesite and basalt; minor graywacke, diorite and quartzite derived from the Modoc Plateau, eastern Klamath Mountains, and Cascade Ranges.	9	850,000 \$660,000	Sand, gravel, and crushed cobble aggregate.	Seasonal replenishment of some stream bed deposits.  (Averill 1939, pp. 170-171, Shasta Co.; O'Brien 1946, p. 195, Tehama Co.; O'Brien and Braun 1952, pp. 42-44, Glenn Co.)
Chico-Oroville-Marysville area. (East side of Sacramento River in Butte, Yuba, and Sutter Counties.)	Chico and Butte Creeks; Feather and Yuba Rivers; minor tributaries.	Recent stream bed and river bar alluvium; dredger tailings.	Andesite, basalt, quartzite, and gneiss derived from the southern Cascade Ranges, and northern Sierra Nevada; vein quartz, quartzite, meta-andesite and basalt, diorite, gneiss, sandstone, and schist derived from the northern Sierra Nevada.	8	1,000,000 Undetermined	Sand and gravel and crushed cobble aggregate; railroad ballast, concrete pipe aggregate; minor filter and sandblast sand and roof granules.	Suction dredges obtain sand from bed of Yuba River. Gold dredger tailings on Butte Creek crushed for railroad ballast. Seasonal replenishment of some stream deposits.  (O'Brien 1949, pp. 435-439, Butte Co.; O'Brien 1952A, pp. 153-154, Yuba Co.)
Woodland-Winters area. (West side of Sacramento River in Yolo County.)	Cache and Putah Creeks.	Recent stream bed, gravel bank, and terrace alluvium.	Meta-sandstones, sandstones, cherts, meta-volcanic rocks, and vein quartz derived from the southeastern portion of the northern Coast Ranges.	5	1,200,000 \$1,020,000	Sand and gravel for aggregate, fill, road surfacing.	Few boulders or cobbles present in most pits, hence little crushed stone produced.  (O'Brien 1950, pp. 425-431, Yolo Co.)
Sacramento area. (East side of Sacramento River in Sacramento County.)	American and Sacramento Rivers, and adjacent flood plains.	Pleistocene (Victor formation) and Recent flood plain terrace deposits; stream bed and bar alluvium.	Mainly metamorphosed basic igneous rocks and quartzitic meta-sedimentary rocks, with minor vein quartz, plutonic and extrusive igneous rocks derived from the western flank of the central Sierra Nevada.	12	6,550,000 \$4,700,000	Sand, gravel, and crushed cobbles for aggregate; much plaster and concrete sand; road surfacing and fill.	Large tonnage produced for Folsom Dam project, 1953-54. Suction dredges recover sand from American River bed, which is seasonally replenished. Many pits are quarried from below the water table. Deficiency of finer sizes overcome by grinding coarse sand in rod mill. Little or no potentially reactive material. Placer gold recovered at several plants.  (Carlson 1955, pp. 153-170, Sacramento Co.)
Central California Ukiah-Healdsburg-Petaluma area. (North San Francisco Bay region, in Mendocino, Sonoma, Napa, Solano and Marin Counties.)	Russian River and minor tributaries	Recent stream bed and river bar alluvium.	Mainly Jurassic graywacke and other sandstones, serpentine and jasper derived from the northern Coast Ranges.	6	1,000,000 Undetermined	Sand, gravel, and crushed cobble aggregate.	Seasonal replenishment in some deposits. Minor amounts of potentially reactive volcanic and chert fragments.  (Davis 1948, pp. 184-188, Napa Co.; Honke and Ver Planck 1950, pp. 105-113, Sonoma Co.; O'Brien 1953, pp. 367-370, Mendocino Co.; Ver Planck 1955, pp. 237-251, Marin Co.)



## Summary of sand and gravel producers of California.—Continued.

Main producing areas <sup>1</sup>		Types of deposits	Type and source of rocks present	Commercial producers active (1953) <sup>2</sup>	Approximate total annual output (1953) <sup>3</sup> (short tons; value)	Main products <sup>4</sup>	Remarks, references <sup>5</sup>
Marketing area	Locations of deposits						
<b>Central California—Continued</b>							
San Jose and San Francisco Bay areas. (West side of San Francisco Bay in San Francisco, San Mateo and Santa Cruz Counties.)	Zayante Creek between Olympia and Felton; near Soquel (Santa Cruz County).	Bedded friable Tertiary, arkosic marine sandstone.	Uniformly graded, light-colored sandstone, with minor chert and shale fragments, all of the upper Miocene Santa Margarita formation exposed in the central Coast Ranges.	5	1,000,000 Undetermined	Concrete, plaster sand; various special sands.	Little or no cobbles for crushed stone. Most sand is obtained in 65 and 100 mesh sieves. Friable sandstone quarried, without blasting, by dragline scrapers.  (Hubbard 1943, pp. 50-52, Santa Cruz Co.).
San Jose and San Francisco Bay areas. (South end of San Francisco Bay in San Francisco, San Mateo and Santa Clara Counties.)	Coyote, Los Gatos, Guadalupe, and Carnadero Creeks; west side of Santa Clara Valley, between Los Gatos and Gilroy. (Santa Clara County).	Recent stream bed and river bar alluvium.	Arkosic sandstone, chert, shale, basalt, gabbro, and quartz fragments, derived from the Cretaceous (?) Franciscan formation of the central Coast Ranges.	6	1,000,000 \$700,000	Sand, gravel, and crushed cobble aggregate, fill, minor filter gravel.	Seasonal replenishment of most deposits. Most creeks flow intermittently. Most deposits worked only to 30-foot depth.  (Davis and Jennings 1954, pp. 373-381, Santa Clara Co.).
San Francisco Bay area. (East side of San Francisco Bay, in Alameda and Contra Costa Counties.)	Niles-Centerville area; Alameda Creek (Alameda County); Livermore-Pleasanton area; Arroyo del Valle and Arroyo Mocho (Alameda County).	Uplifted alluvial cone of ancient stream course. (Niles area); deep valley-fill, river and fan alluvium (Pleasanton area).	Graywacke and arkosic sandstones, diabase, basalt, serpentine, chert, vein quartz, and glaucophane schist derived from the Cretaceous (?) Franciscan formation on the east side of the central Coast Ranges.	7	5,600,000 \$6,000,000	Sand, gravel, and crushed cobble aggregate, fill, ballast, and various specialty products.	Creek bottom deposits in part replenished during rainy season. Layers of clay must be discarded. Deeper pits quarried below water table. Reserve alluvium reported at least 1,000 feet deep in the Niles area and at least 300 feet deep in the Pleasanton area, but coarse boulders increase with depth. Excess pea-gravel crushed to sand.  (Davis 1950, pp. 318-337, Alameda Co.).
Tracy-Modesto-Merced area. (Central San Joaquin Valley in San Joaquin, Stanislaus and Merced Counties.)	Corral Hollow Creek, Calaveras, Stanislaus, and Mokelumne Rivers (San Joaquin County); Orestimba Creek and Tuolumne River (Stanislaus County); Bear, Los Banos, and Mariposa Creeks, and Merced River (Merced County).	Terrace, bar, stream channel, dry creek bed, and alluvial fan deposits of Recent age.	Quartzite, granitic types greenstone, vein quartz, Tertiary volcanic types derived from the west side of central Sierra Nevada; similar types plus arkosic sandstone, chert, and basic igneous fragments derived from the Cretaceous (?) Franciscan and Upper Cretaceous Panoche formations of the central Coast Ranges.	17	3,200,000 \$3,000,000	Sand, gravel, and crushed cobble aggregate, fill, ballast, and various specialty uses. Largely used in road construction.	Minor tonnage shipped from Tracy about 60 miles to San Francisco Bay area. Delta-Mendota Canal borrow material processed for local use as road-surface material. Dredger tailings near Snelling, Merced County, crushed for road construction use.  (Charles 1947, pp. 98-100, Stanislaus Co.; Clark 1955, pp. 60-69, San Joaquin Co.; Davis and Carlson 1952, pp. 231-240, Merced Co.).
Fresno-Visalia-Porterville area. (Central San Joaquin valley, in Madera, Fresno, and Tulare Counties.)	San Joaquin, Kings, Tule, and St. Johns Rivers; various small tributary creeks.	Recent stream bed, dry creek and river bar alluvium.	Granitic, basaltic, and andesitic igneous rocks; gneiss, quartzite, schist, and vein quartz, all derived from the western flank of the central Sierra Nevada.	12	1,200,000 Undetermined	Sand, gravel, and crushed cobble aggregate, concrete pipe aggregate, cobbles for dam facings.	Nearly 4½ million tons of aggregate produced 1940-1942 near Friant for Friant Dam. Preponderance of sand and fine sizes of gravel. Placer gold saved at several plants. Seasonal replenishment of most stream bed deposits.  (Logan 1950, pp. 465-466, Madera Co.; Logan, Braun, and Vernon 1951, pp. 528-531, Fresno Co.).
Bakersfield area. (Southern San Joaquin Valley in Kern County.)	Kern River, Poso Creek.	Recent stream bed, river bar, and dry wash alluvium.	Granitic igneous rocks, quartzitic meta-sediments, meta-volcanics, and schists derived from the western flank of the southern Sierra Nevada.	4	550,000 \$630,000	Sand, gravel, and crushed cobble aggregate.	Seasonal replenishment of some stream bed deposits.



## Summary of sand and gravel producers of California.—Continued.

Main producing areas <sup>1</sup>		Types of deposits	Type and source of rocks present	Commercial producers active (1953) <sup>2</sup>	Approximate total annual output (1953) <sup>3</sup> (short tons; value)	Main products <sup>4</sup>	Remarks, references <sup>5</sup>
Marketing area	Locations of deposits						
Southern California Ventura area. (Coastal plain area in Ventura County.)	Santa Clara and Ventura Rivers.	Recent stream bed, river bar, alluvial plain and terrace alluvium.	Granitic, basaltic, and various dike rocks; sandstone, chert, shale and gneiss derived from the Transverse Ranges.	3	910,000 \$1,150,000	Sand, gravel, and crushed cobble aggregate, fill, road material.	Potentially reactive siliceous Miocene shale present in minor proportions.  (Tucker and Sampson 1932, pp. 271-276, Ventura Co.).
Los Angeles area. (Populous areas in San Fernando and San Gabriel Valleys and in the Los Angeles coastal plain, Los Angeles County.)	Pacoima, Little Tujunga, and Big Tujunga washes (San Fernando Valley area); San Gabriel and Rio Hondo washes (San Gabriel valley area); El Segundo Beach; Palos Verdes Hills, Palmdale area.	Intermittent Recent stream, dry wash, valley-fill and fan alluvium; dune sands, uplifted marine terrace deposits.	Various granitic rock types, granitoid gneiss, and mica-ceous schists derived from the San Gabriel Mountains (Transverse Ranges); quartz-rich ocean beach sands.	26	20,000,000 \$15,000,000	Sand, gravel, crushed cobble aggregate, fill, ballast; wide variety of specialty sands and gravels.	Los Angeles yields about $\frac{1}{2}$ of the state's total of sand and gravel. San Fernando and San Gabriel Valley deposits quarried above water table (maximum depth about 200 feet) similar but more weathered, material reported as deep as 1,000 feet. Zoning restrictions and encroaching housing limit available reserve acreage. Little or no seasonal replenishment. Little or no reactive fragments.  (Gay and Hoffman 1954, pp. 534-551, 553-556, Los Angeles Co.; Lowe 1949, pp. 1-9).
San Bernardino-Pomona-Riverside area. (Eastern San Gabriel and San Bernardino Valleys in San Bernardino and Riverside Counties.)	Santa Ana River wash, Lytle, Cucamonga, San Antonio and Temescal Canyon washes; Miraloma fan.	Recent stream bed, intermittent and dry stream washes; valley fill and fan alluvium.	Various granitic intrusive rocks, granitoid gneiss, mica schist, and dike and vein rocks, derived from the San Gabriel and San Bernardino Mountains (Transverse Ranges) and northern Peninsular Ranges.	11	3,000,000 \$3,400,000	Sand, gravel, crushed cobble aggregate; minor specialty products; fine aggregate for concrete blocks.	Valley-fill and fan alluvium reported to be 500 feet or more deep in places. Little or no seasonal replenishment. Particle size appreciably smaller in pits farther from mountains.  (Wright, et al., 1953, pp. 190-196, San Bernardino Co.).
Santa Ana area. (Southern Los Angeles coastal plain area in Orange County.)	Santa Ana River, Santiago Creek.	Recent riverbed bar, terrace and flood plain alluvium.	Various granitic intrusive rocks, sandstone, gneiss, quartzite, basic dike rocks, and vein quartz derived from the San Bernardino Mountains (Transverse Range) and Santa Ana Mountains (northern Peninsular Ranges).	10	3,000,000 \$2,600,000	Sand, gravel, crushed cobble, aggregate, fill, road surfacing, minor specialty sands.	Little or no seasonal replenishment. Encroachment of building threatens reserves.  (Tucker 1925, pp. 69-71, Orange Co.).
San Diego area. (Southern coastal area in San Diego County.)	Sweetwater, Otay, and San Diego Rivers, Murphy and Murray Canyons.	Recent stream bed, dry wash, and river bar alluvium; poorly consolidated Tertiary sandstone and conglomerate.	Mainly andesite, rhyolite, and quartzite, minor granitic intrusive rocks, and vein quartz, derived from the southwestern Peninsular Ranges, and Eocene (Poway) conglomerate and marine terrace deposits on the coastal plain.	20	3,100,000 \$4,300,000	Sand, gravel, and crushed cobble aggregate, fill, road material; various specialty sands.	Public works projects (dams, airfields) account for large proportion of aggregate used since 1950.  (Tucker and Reed 1939, pp. 49-50, San Diego Co.).

<sup>1</sup> Many scattered deposits which supply local requirements of relatively unpopulated districts are not included. Deposits are located as near as possible to marketing areas to minimize transportation expenses. Most material is marketed within 15 miles of its sources; material is hauled by rail and truck as far as 40 miles to the San Francisco Bay consuming area.

<sup>2</sup> From U. S. Bureau of Mines unpublished list of active commercial operators.

<sup>3</sup> Mineral production for 1953 by counties of California: California Division Mines Mineral Information Service, Vol. 8, No. 1, January 1955, pp. 2-4, 10-12.

<sup>4</sup> "Aggregate" refers mainly to portland cement concrete aggregate and asphaltic concrete aggregate, but minor amounts of concrete pipe and concrete block aggregate are commonly included. For details see text on aggregate and special sands.

<sup>5</sup> References to many operations appear in the periodicals "Pit and Quarry" and "Rock Products." Division of Mines reports referred to contain descriptions of individual operations and area summaries arranged by counties. Many of the data on type and source of rock was obtained by personal communications from Harold B. Goldman, of the California Division of Mines (see also Mineral Information Service, December 1955).





FIGURE 9. Photo showing deposit of marine sandstone of Miocene Santa Margarita formation, exposed in the Olympia (Felton) pit of Pacific Coast Aggregates, Inc., Santa Cruz County. This type of well-bedded, loosely consolidated sandstone which contains very few pebbles, is quarried with slack line cable draglines, carryall scrapers, or bulldozers, as shown here.

Cressey and Arundel, Merced County; the Kings River near Sanger, and the San Joaquin River between Hernon and Friant, Fresno County; the Tule River near Porterville, Tulare County; and the Kern River near Bakersfield, Kern County. Few stream deposits are worked on the west side of the valley, the main ones being along Orestimba Creek near Newman, Tuolumne County; and Bear Creek, near Tuttle, and Los Banos Creek near Los Banos, Merced County.

In southern California, dry wash deposits yield most of the sand and gravel aggregate for the principal consuming area, the Los Angeles area. Little Tujunga, Big Tujunga, and Pacoima Washes in San Fernando Valley, about 15 miles northwest of Los Angeles, and San Gabriel and Rio Hondo Washes, in San Gabriel Valley, about 15 miles east of Los Angeles, are the principal sources. Stream-laid deposits along the lower reaches of the Santa Clara River provide sand and gravel for use in Ventura, Oxnard, and Santa Paula, Ventura County. The Santa Ana River and its tributaries are the principal sources of sand and gravel aggregate for San Bernardino, San Bernardino County; Riverside, Riverside County; and Santa Ana, Orange County. The Sweetwater, Otay, and San Diego River courses are sources of sand and gravel consumed as aggregate in the vicinity of San Diego, San Diego County.

Bedded Tertiary sandstone is quarried for use as aggregate (mostly concrete sand) near Felton, Santa Cruz County. The sandstone is a loosely consolidated, friable rock of the Miocene Santa Margarita formation, widely exposed in the area. The sandstone is quarried without blasting by carryalls and bulldozers and readily breaks down during this handling to a relatively pure sand, without crushing. Most of the output from the Felton deposits is shipped by rail nearly 100 miles to

the San Francisco area, where it is blended with sand-deficient aggregate obtained mainly in the East Bay area. In the Palos Verdes Hills, Los Angeles County, clean, friable, bedded sandstone, also of Miocene age, is similarly quarried and processed for local use mainly as concrete and plaster sand.

Beach and dune deposits of sand occur along the coast line, mainly south of San Francisco, but are primarily sources of specialty sands rather than aggregate. Minor proportions of the beach and dune sand obtained in the Monterey Bay and Pacific Grove areas, Monterey County; the El Segundo area, Los Angeles County; and other



FIGURE 10. Photo showing deposit of gold dredger tailings which were stacked in the early 1900s along the Feather River south of Oroville, Butte County. The tailings here are being mined by the Henry J. Kaiser Company. Very little sand remains in the tailings, and none is produced in this operation; the principal product is crushed stone for railroad ballast.





FIGURE 11. Photo showing a large dry-pit operation in river wash alluvium, typical of many large operations in southern California. View is northwest across the pit of Livingston Rock and Gravel Company, San Gabriel Wash, Los Angeles County. Windrows of oversize boulders have been discarded on pit floor.

less productive areas scattered along the coast, are used for plaster and concrete sand.

#### PRODUCTION METHODS

Most of the recent alluvial deposits in California contain cobbles too large for use as gravel, so most sand and gravel plants crush oversize gravel and cobbles for sale as crushed stone. The crushed stone output of many

plants is nearly as large as their output of sand and gravel; an exact comparison of tonnages is impossible because for many years statistics on California aggregate production included a single figure for "sand, gravel, and crushed rock." Because sand, gravel, and crushed stone are produced largely in the same plants, production methods for both types of aggregate are included in this section. Other aspects of crushed stone are discussed in the section on crushed and broken stone.



FIGURE 12. Photo showing suction dredge of Yuba Sand Company, which recovers sand and fine gravel from the bed of the Yuba River near Marysville, Yuba County. When lowered to the river bed, the rotating head on the suction pipe boom (left of dredger) loosens sand and gravel, which is raised by pumps aboard the dredger and forced in water suspension through the floating pipeline ashore for processing.



FIGURE 13. Photo showing the quarrying of river wash materials by power shovel and bottom-dump truck, in pit of Livingston Rock and Gravel Company, San Gabriel Wash, Los Angeles County (see fig. 7). River wash is poorly sorted and poorly bedded. Truck hauls material about half a mile to hopper at plant on rim of pit.





FIGURE 14. Photo showing the quarrying of river wash material by dragline scarifier, power shovel, and conveyor belt, at Largo plant of Consolidated Rock Products Company, in San Gabriel Wash, Los Angeles County. Heavy metal mass dragged up and down 130-foot bank by dragline on upper level loosens material, controlling slope of pit and providing loose material for shovel to excavate. Sectional conveyor belt system, with jaw crusher installation near center of view, is moved periodically to follow progress of excavation. Oversize boulders are discarded on pit floor. Bench at right is remnant of former quarrying system, before scarifier was designed. Conveyor system is nearly half a mile long.

Sand and gravel operations involve (1) quarrying raw material, (2) transporting it to the processing plant, (3) separating it into desired sizes, (4) washing out excessive fine material, (5) removing detrimental materials, and (6) stacking or binning it for sale. The parallel operation of producing crushed stone starts at the first screening, after which oversize is crushed, screened into desired sizes, and stored for sale. Nearly all sand and gravel is washed, but most crushed stone is processed and sold dry.

Haulage to the plant, rarely more than half a mile, is commonly by dump truck or by belt conveyor; seldom by rail. At most plants raw material is delivered to surge piles, to be processed when desired.

In the plant all material is first separated on a coarse scalping screen, into sand and gravel (top size ordinarily about  $1\frac{1}{2}$  inches), and oversize, to be crushed. Mechanical vibrating screens of one, two, or three decks are used

throughout nearly all plants; trommel screens are used for scalping at a few small plants.

The sand and gravel is further classified on successive screens into various size groupings. Excessive fines are washed out by streams of water directed against the screens and by log, rake, and spiral types of sand washing and classifying machines. Approximately ten gallons of wash water per minute is required for each ton of material produced per hour, or 600 gallons per ton (Walker 1954, p. 170). Washed aggregate is commonly piled to drain dry before removal to bins for sale.

Some sand and gravel deposits otherwise satisfactory for aggregate use contain harmful proportions of detrimental substances such as clay, unsound shale fragments, or reactive materials. If demand is sufficient to

*Truck haulage rates for common rock products.\**

Haul (miles)	Cost (cents per ton)	Haul (miles)	Cost (cents per ton)	Haul (miles)	Cost (cents per ton)
0-1	22	14-16	95	60-65	261
1-2	27	16-18	103	65-70	279
2-3	34	18-20	110	70-75	296
3-4	39	20-23	119	75-80	314
4-5	44	23-26	128	80-85	332
5-6	49	26-30	138	85-90	350
6-7	56	30-35	155	90-95	368
7-8	61	35-40	173	95-100	384
8-9	66	40-45	191	100+	add 18 cents
9-10	71	45-50	208		for each 5
10-12	80	50-55	226		miles or
12-14	87	55-60	244		fraction.

\* Rate for dump truck delivery of sand, gravel, and crushed rock; minimum load is 8 tons. Cost includes loading, hauling and dumping charges. (From California Public effective January 10, 1951, between points in southern California.)



FIGURE 15. Photo showing the quarrying of river flood-plain material (Pleistocene Victor formation) from beneath water level by dragline and bottom-dump truck, at pit of Perkins Gravel Company, Sacramento County. Truck hauls about a mile to plant.





FIGURE 16. Photo showing the quarrying of river flood-plain deposits in Arroyo Valle, Livermore Valley, Alameda County, at the Radium plant of the Henry J. Kaiser Company. Monighan dragline (left) with 10 cubic yard bucket excavates material from as deep as 30 feet below water, and unloads into floating hopper (center) for mile-long haul by conveyor belt to plant. Crawler dragline (upper center), with 5 cubic yard bucket, excavates bank material down to level on which Monighan operates. *Photo courtesy of Henry J. Kaiser Company.*

warrant the expense involved, material from such deposits may be beneficiated, or processed to reduce the detrimental components to an acceptable level. Methods or processes commonly used to beneficiate aggregate include heavy-media separation, flotation, selective crushing, and intensive scrubbing and washing.

Throughout most of California aggregate may be readily obtained from deposits that need no beneficiation other than a certain amount of washing to remove excess

clay and fine material. A notable example of successful aggregate-beneficiation is seen at Black Point, Marin County, where acceptable aggregate has been produced since 1954 from the Cretaceous (?) Novato marine conglomerate. Soft cobbles and the soft weathered outer portions of other cobbles are removed by a process of selective crushing and washing. Excess clay is freed and removed in attrition machines, wet cyclones, and spiral classifiers (Ver Planck 1955, pp. 239-242). Specialty



FIGURE 17. Photo showing excavation of river bed gravel by doodlebug dredging unit with dragline excavator, at Madison Sand and Gravel Company operation on Cache Creek, Yolo County. Washing unit, afloat in excavation, separates and stacks material up to 6 inches diameter (left) for use at Monticello Dam; material finer than  $\frac{3}{8}$ -inch is returned to the pond. *Photo courtesy U. S. Bureau of Reclamation.*





FIGURE 18. Aerial view north toward plant and quarry of Torrance Sand and Gravel Company in bedded beach or terrace deposits of Pleistocene San Pedro sand on the southeast flank of the Palos Verde Hills, Los Angeles County. The poorly consolidated sandstone, which generally contains less than 10 percent of particles larger than a quarter of an inch, is excavated by dragline, slackline cable dragline, and bulldozer, and carried by belt conveyor to the plant. Residences are close to the operation, a situation responsible in several districts for friction between home owners and sand and gravel producers. *Photo by Pacific Air Industries, Long Beach, 1955.*





FIGURE 19. Aerial view west along Arrow Highway (right edge), showing two large sand and gravel operations in the San Gabriel River wash near Irwindale, Los Angeles County. In foreground is deep pit of Manning Brothers Rock and Sand Company, with plant, abandoned pit sites, and stockpile area at left. On the far side of Irwindale Avenue, which trends from right to left across the center of the picture, is the pit and plant of Consolidated Rock Products Company's Irwindale operation, one of the largest in southern California. The large, in part brush-covered, excavation (middle distance, at right) is no longer active. The deep L-shaped pit (upper left corner), from which material is brought by belt conveyor to the plant, has been active in the 1950s. Residential buildings are close to all sides of the excavations. *Photo courtesy of Manning Brothers Rock and Sand Company, 1952.*



sand plants in California commonly beneficiate sand to remove clay, iron stains and iron-bearing minerals before the sand can be used for glass-making. Attrition, flotation, wet cyclones, tabling, and magnetic separation processes are in use in various specialty sand plants in the state (see section on specialty sands).

In the crushed stone section of most plants, jaw crushers are used for primary crushers, and cone, gyratory, and roll crushers for secondary crushers. The crushed stone is screened in the same way as the sand and gravel except wash water is rarely used. Where the natural material is deficient in sand as in the Niles-Pleasanton area, rod mills may be used to reduce larger fragments to sand.

Transportation throughout most plants is by belt conveyors, bucket elevators, and gravity. Traveling cranes with clam-shell buckets are in common use in storage yards to load bins or trucks.

Sand and gravel plants in California range from large, integrated operations, capable of sustained production of as much as 1,000 tons per hour, to small, intermittent operations that produce a few tons whenever necessary. Consumer demand, capitalization, and distance from market as well as the size and nature of the deposit determine the size of sand and gravel plants. Most of the larger plants are completely mechanized, and some produce as many as 15 sizes of aggregate. Small operations are less flexible and the simplest produce only untreated pit-run material. Several of the plants that operate in stream-deposited gravels extract gold from the aggregate during washing. The largest of these are at Azusa in Los Angeles County, and Fair Oaks in Sacramento County.

#### PRICES, COSTS, AND MARKETS

Aggregate producers are divisible into two main classes: (1) commercial producers, who have permanent plants and sell on the open wholesale and retail market; and (2) government and contractor producers, who accept contracts to provide aggregate for particular large-scale government projects, such as dams, and operate plants only to fulfill their contracts. In 1953, commercial producers in California sold 43,849,690 tons of sand and gravel aggregate, valued at \$44,602,421, while government and contractor producers sold 14,579,838 tons valued at \$8,621,782 for use on public projects (Otis and Shupp 1956, p. 8). Price, cost, and marketing data in this section apply primarily to commercial operations.

Sand and gravel for aggregate is by nature a large-tonnage commodity of low unit cost. The national average price to consumers for commercially produced washed, screened, and otherwise prepared sand and gravel was \$1.04 per ton in 1953, compared with 75 cents per ton for unprepared bank-run material (Otis and Shupp 1955, p. 2). In California, commercial prepared sand and gravel ranged in value from about \$1.00 to about \$1.80 per ton, f.o.b. plant, in the main producing areas in 1955.

Differences in the selling prices for different types of aggregate in general reflect the relation between supply and demand for particular types of aggregate, rather than differences in production costs for different products. In 1955 the size distribution of the raw material

supplied in the Los Angeles area was nearly compatible with the current demand. A shortage of finer sizes existed in the San Francisco and Sacramento areas. The proportion of fine material may be augmented by grinding larger particles, but the reverse problem is harder to overcome. Demand for certain types of aggregate is affected by changes in engineering techniques and specifications. For example, crushed particles were formerly preferred to rounded particles for portland cement concrete aggregate, and a surplus of gravel resulted. Later reversal of this specification resulted in a surplus of crushed stone. More recently, the greatly expanded use of asphaltic concrete has increased the demand for crushed stone, and tended to equalize the demand for crushed and uncrushed aggregate.

Prices quoted are f.o.b. plants because rates for delivery to consumers are set by the State of California Public Utilities Commission, and are standard throughout wide areas. In southern California most aggregate is delivered by dump truck, and rates per ton delivered are set for three optional bases of hauling: (1) per mile of haul; (2) on zonal basis, from designated producing to designated consuming zones; or (3) on an hourly basis for haulage time consumed. In northern and central California railroad haulage is more used than in southern California. Rail rates are published for point-to-point haul from plant to delivery yards, whence trucks haul to the job. In recent years truck haulage directly from the plants has increased at the expense of rail haulage, largely because of the convenience of one-stop to-the-job delivery, as well as increased railroad haulage rates.

*Prices of sand, gravel, crushed rock in Los Angeles area.\**

Product	F.o.b. price (per short ton)	
	San Gabriel Valley plants	San Fernando Valley plants
Plaster sand.....	1.20	1.60
Granite sand.....	1.25	1.60
Concrete sand.....	1.15	1.60
No. 1 gravel.....	1.20	1.55
No. 2 gravel.....	1.30	1.60
No. 3 gravel.....	1.60	1.80
No. 4 gravel.....	1.50	1.60
No. 5 gravel.....	1.50	1.80
Rock dust.....	1.30	1.60
Crushed rock base.....	1.30	1.60
No. 1 crushed rock.....	1.45	1.75
No. 2 crushed rock.....	1.10	1.45
No. 3 crushed rock.....	1.30	1.60
No. 4 crushed rock.....	1.50	1.80
Railroad ballast.....	1.10	1.60

\* Retail list prices (f.o.b. plants) in 1955 of main products sold by one of the large producers of sand, gravel, and crushed rock, in the Los Angeles area. Trucking costs must be added to obtain delivered prices.

As the costs of producing sand and gravel aggregate differ markedly from plant to plant and from district to district within California, generalized cost estimates on a state-wide, or even district-wide basis, are difficult to arrive at and not particularly meaningful. Total production costs per ton of aggregate are low enough that even slight differences in operating costs of competitive plants may determine their commercial success or failure.





FIGURE 20. Aerial photo of parts of the San Gabriel and Rio Hondo Washes, San Gabriel Valley, Los Angeles County, showing the most productive sand and gravel deposits in California. See fig. 21 for identification of features shown. *Photo by Pacific Air Industries, Long Beach, 1952.*

Variable factors in establishing costs include: (1) scale of operation; (2) location (availability of power, water, and labor; length of haul from pit; accessibility to market); (3) nature of raw material (relative abundance of various usable sizes; proportions of fine and oversize materials; quality of stone; consolidation or cementation of deposit; position of water table; possible seasonal replenishment; depth of overburden); (4) nature of operation (type, size, and general condition of

mining, hauling, crushing, screening, washing, conveying, drying, stockpiling, loading, and delivering equipment); (5) miscellaneous factors (royalties to owners; taxes, depletion of reserves; civic regulations as to zoning, hauling, dust, noise, and safety devices such as high fences and slope-control equipment).

For example, a large completely mechanized plant can produce 1,000 tons of washed and crushed products per hour at a lower cost per ton than a 100-ton-per-hour



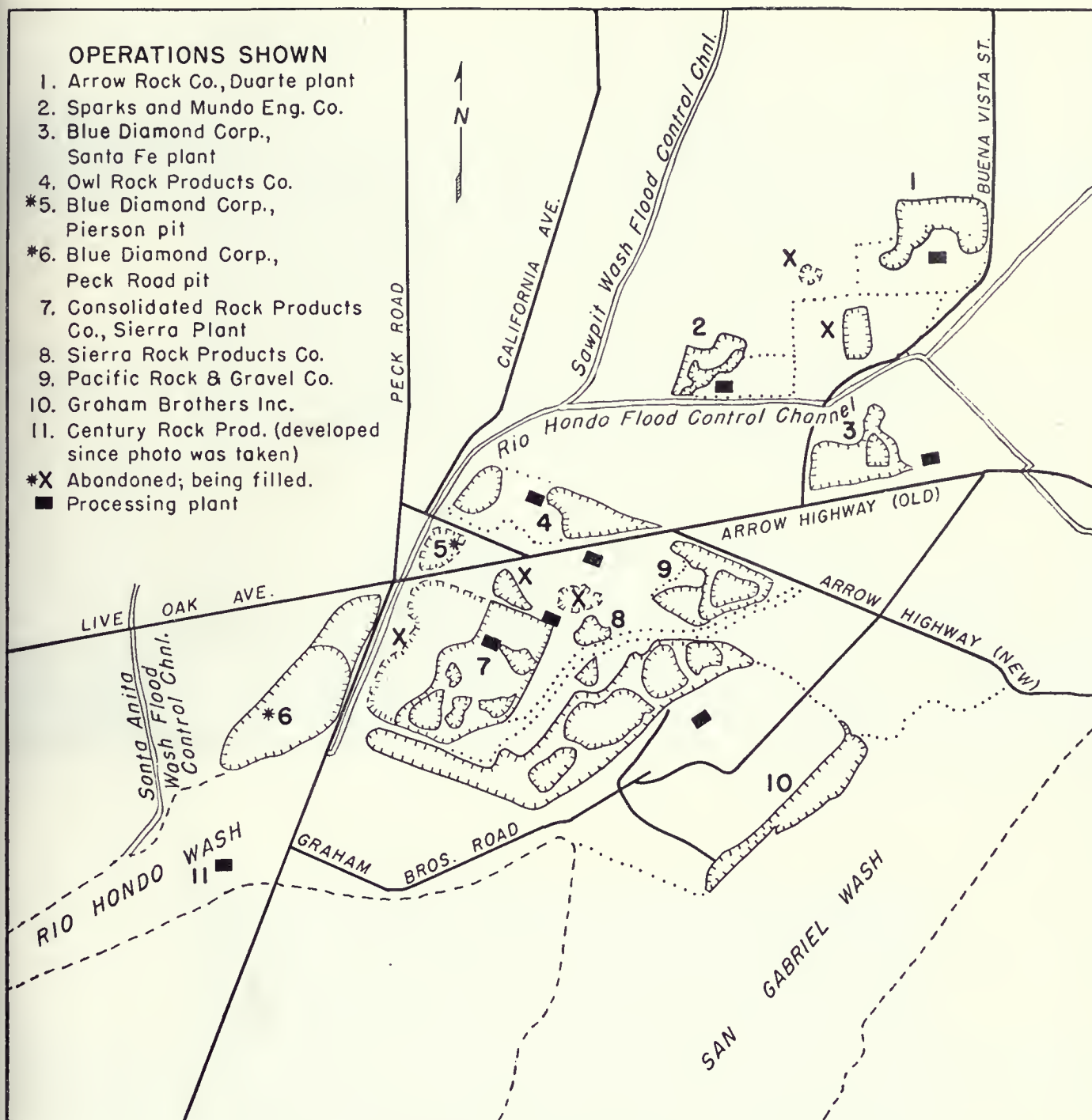


FIGURE 21. Sketch to identify features shown on aerial view of San Gabriel Valley sand and gravel district (see fig. 20).

plant producing the same products in the same area. In 1955 a small portable plant could produce under optimum conditions, uncrushed unwashed bank-run material for as little as 40 cents per ton, appreciably less than either permanent plant above. The cost of the large tonnages of aggregate supplied by contractors to specific projects such as dams was in the range 50 to 75 percent of the listed retail prices.

Zoning restrictions are an increasingly difficult problem for aggregate producers in urban areas such as the

San Gabriel and San Fernando Valleys near Los Angeles. Although large volumes of sand and gravel exist adjacent to active pits in those areas, dwellings, public and industrial buildings, and roads are so rapidly covering the areas that most of the material that would otherwise be considered as reserves was unavailable to quarrying in 1955. When present pits are exhausted to practical depths and limits, producers will be forced to seek new sources, mostly in outlying districts, and the cost of aggregate to consumers will correspondingly increase.





FIGURE 22. Photo showing one of the most modern of the larger sand and gravel plants in the central California area, the Pacific Coast Aggregates, Inc., Eliot plant 104 near Pleasanton, Alameda County. Raw material is obtained from river flood-plain deposits of Arroyo Valle, in Livermore Valley. *Photo by Mort D. Turner.*



FIGURE 23. Photo showing the Irwindale plant of Consolidated Rock Products Company, in Los Angeles County. This is one of the largest sand and gravel plants in the southern California area. Raw material is obtained from deposits in San Gabriel Wash.



FIGURE 24. Photo showing the Santa Fe plant of Blue Diamond Corporation, in San Gabriel Wash, Los Angeles County. This is one of the most compact of the large sand and gravel plants in California. Raw material arrives by belt conveyor (lower left) and, after being processed in the upper decks of the structure, is stored in metal bins beneath for gravity loading of trucks. Reserve finished materials are stacked by belt conveyor (center left), for future sale.





FIGURE 25. Photo showing one of many medium-sized sand and gravel operations, such as provide aggregate for scores of smaller cities and towns in California. The plant shown is that of the Madison Sand and Gravel Company, which processes streambed material from Cache Creek near Madison, Yolo County. *Photo courtesy U. S. Bureau of Reclamation.*

The principal markets for most commercial producers of aggregate generally are within areas of greatest population density. Tremendous tonnages of concrete are also used in highway projects, dams, and canals scattered throughout much of the state. Contractors commonly establish temporary aggregate processing plants at nearby deposits for the duration of such projects.

The present economic limit to the distance sand and gravel can be hauled for use as aggregate differs in different parts of the state. In the Los Angeles area aggregate is rarely hauled farther than 20 miles; in the San Francisco area the nearest sources are about 40 miles from the main consuming centers; most smaller centers of aggregate consumption in the state obtain aggregate from sources less than 25 miles distant. If suitable aggregate is not available near a new market, the user may pay the high haulage costs from distant sources, or accept inferior aggregate from closer deposits.

Little aggregate is sent out of the state except from a few producers near the state's borders: As long as the present high construction rate continues, the commercial

sand and gravel aggregate industry seems assured of strong markets. Completion of planned projects by such agencies as U. S. Army Corps of Engineers, U. S. Bureau of Reclamation, and California Division of Highways should continue to provide a large market for government and contractor aggregate producers.

#### RAILROAD BALLAST

More than 90 percent of the ballast produced and used in California is crushed stone rather than sand and gravel, because the interlocking of angular fragments produces a greater stability. A large proportion of sand gives added stability to ballast composed of uncrushed gravel (see discussion of ballast in section on crushed and broken stone.)

Railroads purchase less than 1 percent of the sand and gravel produced in California for use in ballast and fill. Most of the railroad companies operate their own ballast pits, for which production figures are unavailable. Several of the larger commercial gravel pits in various parts of the state are equipped with rail loading facilities



FIGURE 26. Photo showing the Seaside Beach plant of the Monterey Sand Company, on Monterey Bay, Monterey County. This plant processes aggregate sand from the adjacent beach deposit. Sand is obtained from below and above the sea level by slackline cable dragline scrapers.





FIGURE 27. Photo showing a small portable plant such as is commonly used by contractors to obtain sand and gravel from local sources for projects in outlying districts. This plant is producing road-base materials for use on the Monticello Dam project, Napa County. *Photo courtesy U. S. Bureau of Reclamation.*

and sell the coarser grades of material processed for use as aggregate. In 1952, railroads purchased 181,257 tons of gravel, valued at \$121,851; and 1,440 tons of sand valued at \$792, in California, for use as ballast (Otis and Jensen, 1955, pp. 6, 8).

#### FILL

Undetermined, but very large, tonnages of sand and gravel, as well as other types of rock and earth, are used without binder for various types of fill. The procurement of fill involves mainly availability and economy of recovery. Although quality specifications are virtually nonexistent, excessive organic material is not desirable. Waste material from nearby excavations commonly is used except where requirements of especially good drainage necessitate the use of permeable material such as sand and gravel. When used as fill, sand and gravel is ordinarily of bank-run quality, trucked directly from the excavation to the site of use without processing.

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FIGURE 28. Photo showing the production of aggregate from streambed deposit, at operation of Joe Chevreau, contractor, on Bear River, near Colfax, Placer County. Hydraulic mining for gold in the 1800s caused an unusually large quantity of quartz-rich Tertiary stream gravel to be washed from upstream tributary gulches into Bear River, and provided a source of high-quality aggregate sand and gravel.

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## SHALE, EXPANSIBLE

By B. H. ROGERS AND CHARLES W. CHESTERMAN

Although the heating of claystone and shale to produce expanded shale lightweight aggregate has been practiced in the United States since 1913, the large-tonnage production of such material in California has developed only since 1945. In 1956, five plants in California were producing expanded or burned shale aggregate. Expanded and burned shale are used in many concrete products including a variety of prefabricated units such as wall, floor, and ceiling slabs, structural beams and pillars, and masonry blocks, and structures made from concrete poured in situ.

*Terminology and General Geology.* Shale is commonly defined as a moderately indurated, laminated or fissile sedimentary rock composed mostly of mineral particles in the size range of clay or silt. When used with reference to raw material for the production of lightweight aggregate, however, the phrase "expansible shale" ordinarily embraces virtually any fine-grained sedimentary or metasedimentary rock that expands when heated under suitable conditions. Classed as expansible shale in an industrial sense, therefore, is much massive material that ordinarily would be identified as claystone or siltstone as well as some occurrences of the metamorphic rock slate. In the discussion to follow, the term "shale" will refer to the general group of fine-grained, clay-rich sedimentary rocks.

Most of the shale in California is in sedimentary formations that were deposited in the Jurassic to Recent time interval. The pre-Jurassic fine-grained sedimentary rocks generally have been metamorphosed to argillite, slate or phyllite. As the Mesozoic and Cenozoic seas of California were confined mostly to the area west of the Sierra Nevada, and west of the Mojave and Colorado Deserts, shale-bearing formations are most abundantly exposed in the Coast Ranges, the western part of the Transverse Ranges, and the western slopes of the Peninsular Range.

Reconnaissance sampling and testing of shale deposits by the California Division of Mines indicates that deposits of expansible shale, potentially suitable for industrial use, occur mostly in marine sedimentary formations of Jurassic, Cretaceous, Eocene, and Pliocene ages. Most of the shale in these formations will expand. Shale of Miocene age is abundant but ordinarily is too siliceous to permit a suitable expansion. The Quaternary sedimentary units of California generally consist of coarser non-expansible detritus.

The commercial value of any single deposit can be determined only by (1) a very thorough testing of both the shale and the concrete made from it, and (2) considerations of accessibility, distance from markets, and ease of mining.

In northern California most of the expansible shale of potential commercial interest appears to be confined to formations of Jurassic and Cretaceous ages. It is especially abundant in the Knoxville and Horsetown formations, of Upper Jurassic-Lower Cretaceous age, which are exposed in a north-trending belt about 150 miles long and as much as 20 miles wide. This belt extends

from Redding to San Francisco along the west side of the Sacramento Valley. The shale-bearing units are thousands of feet thick, and mineable bodies many hundreds of feet thick and thousands of feet in exposed length occur in the area between Paskenta and Wilbur Springs and in the area northeast of Napa.

Shale of Lower Cretaceous age also is abundant along the south and east flanks of Mount Diablo, Contra Costa County, and bodies hundreds of feet thick are common in the area south of Clayton. In the Diablo Range, along the east side of the Santa Clara Valley, shaly units of Upper Jurassic-Lower Cretaceous age form belts as much as 4 miles wide and 10 miles long. Although the shale is interlayered with sandstone, mineable shale bodies are as much as 1,000 feet thick and half a mile in exposed length. In the San Jose region of Santa Clara County, shale interbedded with sandstone occurs in the Knoxville formation of Upper Jurassic age and the Berryessa formation of Lower Cretaceous age. Here, it forms bodies as much as 100 feet thick.

In many places in central and northern California, the Lower Cretaceous formations are overlain by Upper Cretaceous beds that also are shale-bearing. The Upper Cretaceous shale, however, is commonly interbedded with sandstone so that the shale bodies are generally less than 10 feet thick and would be difficult to mine. In southern Napa County, north of Vallejo, however, an Upper Cretaceous shale body, about 70 feet thick, is mined by the Basalt Rock Company.

The Franciscan formation of probable Jurassic or Lower Cretaceous age also contains expansible shale, but this is commonly interbedded with sandstone. The Fran-



FIGURE 1. Map of California showing location of expanded shale and burned shale operations.



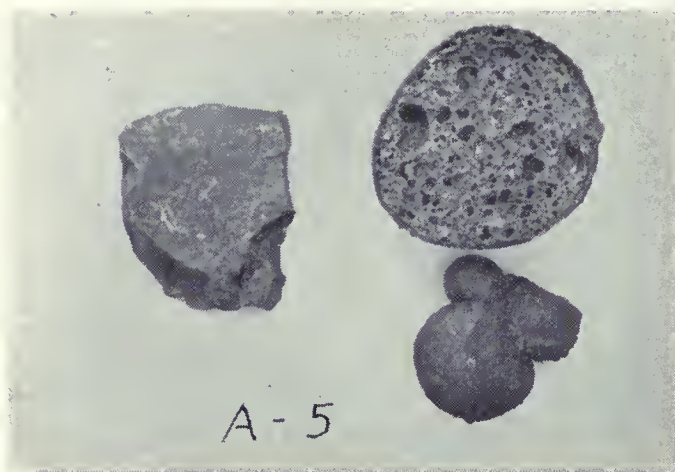


FIGURE 2. Unfired and expanded shale. Upper right, interior of typical expanded shale fragment. Upper left, unfired shale fragment. Actual size.

eisean formation is the source of the raw material expanded by the McNear Brick Company at McNear Point in Marin County. Here the shale is removed from a body about 150 feet thick.

In southern California, expansible shale occurs in deposits of Cretaceous, Eocene, Miocene, and Pliocene ages, especially the Espada formation of Lower Cretaceous age, the Holtz shale members of the Ladd formation of Upper Cretaceous age, the Cozy Dell, and the Rose Canyon member of the La Jolla formation both of Eocene age; the Sycamore Canyon member of the Puente formation, the Lockwood clay and the Capistrano shale, all of Miocene age; and the Pico formation of Pliocene age.

The Espada formation occurs in belts as much as 3 miles long on the north side of the Santa Ynez Mountains between Buellton and Santa Barbara, in Santa Barbara County. Here shale is interbedded with sandstone, but the sandstone layers are thin and sparse and individual bodies of shale are 100 feet thick or more.



FIGURE 3. Basalt Rock Company expanded shale plant. Napa Junction, Napa County. Photo courtesy of Basalt Rock Company.

The Cozy Dell formation is extensively exposed in a wide belt of Eocene rocks that underlies much of the Santa Ynez Mountains from Point Conception eastward for about 70 miles in both Santa Barbara and Ventura Counties. The shale of the Cozy Dell formation is interbedded with sandstone but mineable bodies hundreds of feet thick are common and were noted in both the Ojai and Santa Barbara areas.

The Chico formation forms a large part of the Simi Hills, which lie west of Chatsworth in Los Angeles and Ventura Counties. Here this formation consists mostly of sandstone and conglomerate, but a body of shale about 150 feet thick and as much as 2 miles in exposed length lies near the crest of Santa Susana Pass.

Large areas north of the Santa Clara Valley in Ventura County, are underlain by the Pico formation, especially the Mud-pit member, which here contains a high portion of shale. Large bodies of shale are common within this region. One of these, which is at least 200 feet thick, is quarried by the Rocklite Company near the city of Ventura.

Exposures of the Lockwood clay lie in an area of about 4 square miles near Frazier Park in the northeastern part of Ventura County. This shale is mined and expanded by Ridgelite Products Company, and is at least 120 feet thick in the quarry.

The Sycamore Canyon member of the Puente formation outcrops extensively in the Chino Hills between Puente and the Prado Dam. In this member shale is interbedded with sandstone, but bodies of shale 300 or more feet thick and many hundreds of feet in exposed length occur north and west of Prado Dam.

The Holtz shale member of the Ladd formation outcrops in belts as much as one mile long on the southwestern slopes of the Santa Ana Mountains. In this area the shale is interbedded with inch-thick sandstone and minor limestone layers. A shale body as much as 1,000 feet thick and of possible commercial interest was observed in Silverado Canyon, Orange County.

The Capistrano formation underlies an area of 40 to 60 square miles near San Juan Capistrano, Orange County, and contains bodies of shale that are hundreds of feet thick. Exposures of shale-bearing formation of Upper Cretaceous age about  $1\frac{1}{2}$  miles square are near Carlsbad. Although the shale is interbedded with sandstone and limestone, zones 25 to 50 feet thick and containing 80 percent shale are common.

North of the city of San Diego, the Rose Canyon shale member of the La Jolla formation is extensively exposed. In this unit the shale is interbedded with sandstone and conglomerate but occurs in mineable bodies as much as 150 feet thick and many hundreds of feet in exposed length.

**Treatment.** Rotary kilns are employed in the manufacture of expansible shales on a commercial basis. First the raw material is crushed. Then, if rounded and coated particles are to be produced, it is screened and graded, and only material of the desired size range is fed into a rotary kiln. The rotation rate, pitch, and temperature characteristics of the kiln are adjusted to produce optimum expansion of any one size range. In some plants, the kiln feed is not carefully graded, but later the expanded material is crushed to angular, uncoated particles and then graded as the final stage.





FIGURE 4. General view of the Rocklite expanded shale plant, Ventura County. Quarry-run shale is hauled to crusher (C) where it is sized. The sized shale is placed in storage bins (B) and fed at regular rate into the rotary kilns (K) where it is expanded. Observer faces northeast.

As the shale fragments pass through the kiln they encounter progressively increasing temperature zones in which occur the gas-forming, glass-forming, and expansion stages of reactions (Bauer, 1948, p. 71). Since these reaction periods overlap each other in the temperature-time scale, they cannot be designated as definite stages. Certain stages, however, may be designated in order of increasing temperature. Stage 1 (up to 300° F.) is the drying period when all moisture that is held mechanically in the shale is driven off. In stage 2 (250° to 625° F.), the first of two dehydration periods, the hygroscopic or colloidal water is removed. In stage 3 (725° to 1470° F.), the second dehydration period, all water of hydration (e.g., in hydroxides and kaolin) is removed from the shale fragments, which by now are well into the gas-forming section of the kiln. Stage 4 (800° to 2130° F.) is the oxidation period, a very important gas-forming stage in which carbon, sulfur, and iron are oxidized. Stage 5 (925° F. and upward) is the dissociation-reduction period when calcium and magnesium carbonates and sulfates are dissociated, and ferric iron reduced to ferrous iron. Stage 6 (1470° F., and upward) is the vitrification period and the beginning of the glass-forming stage.

Stage 7 (2000° to 2350° F.) is the pyroplastic stage. By this time the shale fragments have passed through the gas- and glass-forming stages and are beginning to



FIGURE 5. Mining shale from bench at east end of Rocklite quarry, Rocklite Company, Ventura County.





FIGURE 6. General view of the Ridgelite Products Company burned shale operation near Frazier Park, Ventura County. Shale (claystone) is obtained from thick Miocene beds at quarry (Q) and processed at plant (P). Present operation utilized one rotary kiln 100 feet long and 8 feet in diameter. A second kiln of the same size and capacity is standing unassembled. Observer faces northeast.

expand. Stage 8 is the melting period, a stage where the expanded fragments suffer a loss of structure and shape, and develop the external skin (Bauer, 1948, pp. 71-73). Stages 2 to 5 primarily involve gas-formation; the 6th glass-formation, and the 7th and 8th the expansion of the shale fragments.

Several factors determine the heat expanding properties of shale. Among them are (1) mineralogical and chemical composition of the clay minerals and accessory minerals, and (2) the gas- and glass-forming constituents of the shale. The most common gas-forming constituents are carbon, sulfur, and water. The glass-forming constituents are salts of sodium, potassium, lead, copper, and boron (the low-temperature fluxing materials), and the silicate minerals, such as the feldspars and clay minerals (the higher temperature fluxing materials).

Shales generally differ from one another in the proportions of glass- and gas-forming constituents, and will, therefore, react differently in the kiln.

A typical particle of expanded shale is rounded or sub-rounded and consists of a dark-gray central part which resembles frothy glass. This center is surrounded by a dense, partially fused, reddish-brown surface zone which forms a tough, relatively impervious shell.

The weight per unit volume of expanded shale varies with the size of the particle. The larger particles have a lighter weight per unit volume than the smaller ones. A mixture of expanded shale particles weighs about one-half as much per unit volume as a comparable mixture of sand and gravel. Concrete made with expanded shale weighs about one-third less than ordinary sand and gravel concrete.

*Expanded Shale Operations in California.* In 1956, expanded or burned shale were being produced at five plants in California, two in the northern part of the state and three in the southern part. These were producing a total of about 200,000 to 300,000 cubic yards of expanded shale annually.\*

\* These figures are estimates based on knowledge of plant capacities. The range is calculated on the basis of one-half to two-thirds capacity operation during a 250-day year.

Northern California was being supplied by material quarried and processed in southern Napa and eastern Marin Counties by the Basalt Rock Company and the McNear Brick Company respectively. The operation in Napa County uses shale obtained from the Upper Cretaceous Chico formation and was begun in 1953. In Marin County the Franciscan formation is quarried and expanded near San Rafael. This operation was begun in 1932.

In southern California the Rocklite Company and the Ridgelite Products Company are in Ventura County, and the Airox Company is in Santa Barbara County. The Rocklite operation uses shale from the Mud-pit member of the Pico formation of Pliocene age at a locality in the Ventura oil field. This operation has been active since about 1940. The Ridgelite Products Company operation which was begun in about 1952 uses claystone from the Lockwood clay of Miocene age at a locality near Frazier Park. This company produces a burned aggregate by heating claystone at a temperature of about 2000° F. The particles do not change in volume or shape, but lose weight primarily through the escape of moisture and volatiles in the claystone. The Airox Company, with a plant and quarry near Casmalia, Santa Barbara County, also produces a lightweight aggregate by burning an oil-saturated diatomaceous shale of the Miocene Sisquoc formation. Although the product is not an expanded shale, it is a lightweight material produced by burning the natural bitumen while the shale is spread in open piles.

Although the crushing and sizing processes, the rotation rate and pitch of the kilns, and the time required for the shale to traverse the kilns differ slightly from plant to plant, the only major difference in the plants that actually expand shale is in the numbers and sizes of the kilns employed. In 1955, the Basalt Rock Company was employing four kilns 125 feet long and 8 feet in diameter; the Rocklite operation, three kilns 125 feet long and 8 feet in diameter, and another 75 feet long and 6 feet in diameter; the McNear Brick Company, two kilns 80 feet long and 6 feet in diameter; the Ridgelite Products Company, one kiln 100 feet long and 8 feet in diameter. In 1954 these operations probably produced



FIGURE 7. General view of the south face of Ridgelite Products Company shale (claystone) quarry, Ventura County.





FIGURE 8. Airox Company's burned shale operation at Casmalia, Santa Barbara County. Bituminous, diatomaceous shale is obtained from quarry (Q), sized at crusher (C), and burned in yard (Y). Burned shale is prepared for aggregate and pozzolan at plant (P). Observer faces southwest.

150,000 to 200,000 yards of expanded shale. For the same year the Expanded Shale Institute estimated that 33 plants in the United States and Canada produced 2,250,000 yards. Early in 1956 the combined production capacity of the four operations in California was about 1500 yards per 24-hour day.

Both of the main types of expanded and burned shale aggregate are being produced in California: (1) aggregate consisting of rounded particles of expanded and burned shale with dense and essentially impervious

shells, and (2) aggregate consisting of angular fragments of crushed expanded shale. The first type involves a crushing and screening of the raw material before it is fired, and is the type produced by the Basalt Rock Company, the Rocklite Company, and the Ridgelite Products Company. The second type is crushed and screened after firing, is similar in appearance and physical properties to natural volcanic cinders and scoria, and is produced by the McNear Brick Company.

**Utilization.** All of the expanded and burned shale companies in California use the material in the production of concrete products. Two of the companies also sell the aggregate on the open market. Most of the aggregate is used in the production of concrete blocks which are made similarly to blocks that contain ordinary sand and gravel or natural lightweight aggregate. The bulk of the burned shale produced by the Airox Company, however, is used in the manufacture of a pozzolan. Most of the blocks are made by the expanded shale companies themselves, and all but one produce concrete products at the sites of the expansion plants. The other operator, the Ridgelite Products Company, transports aggregate about 100 miles from the aggregate plant to the block plant.

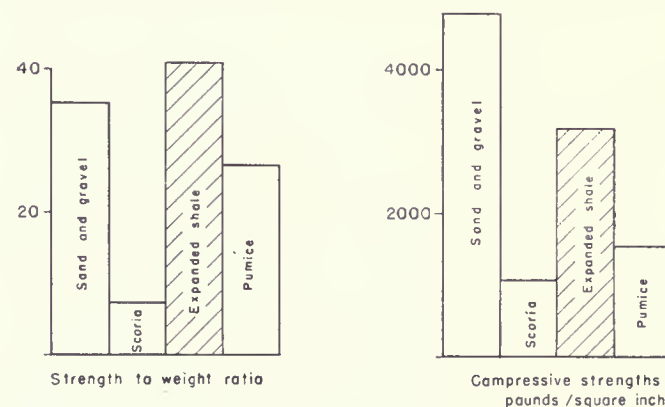


FIGURE 10. Properties of concrete made with five bags of cement per cubic yard of concrete.

The two largest operations produce, in addition to concrete blocks, a variety of concrete products including prefabricated roof, floor and wall panels, structural beams, and units of prefabricated houses, silos, and water tanks.

Expanded and burned shale have invaded the aggregate market to some extent in almost all fields where concrete is used. In addition to blocks and other prefabricated products such as those mentioned above, expanded shale aggregate has been used as well in monolithic concrete structures such as the Statler Hotel in Los Angeles and the Equitable Life Assurance Society Building in San Francisco. Because the expanded shale concrete is lighter, substantially less steel was used in these buildings than had ordinary sand and gravel aggregate concrete been employed. The higher cost of expanded and burned shale aggregate was largely offset by the lower cost of steel reinforcement. For most heavy construction, however, in which both weight and very high strength are necessary, sand and gravel probably will continue to be used. Lightweight aggregate is porous,

Properties of concrete with compressive strength 2000 P.S.I.

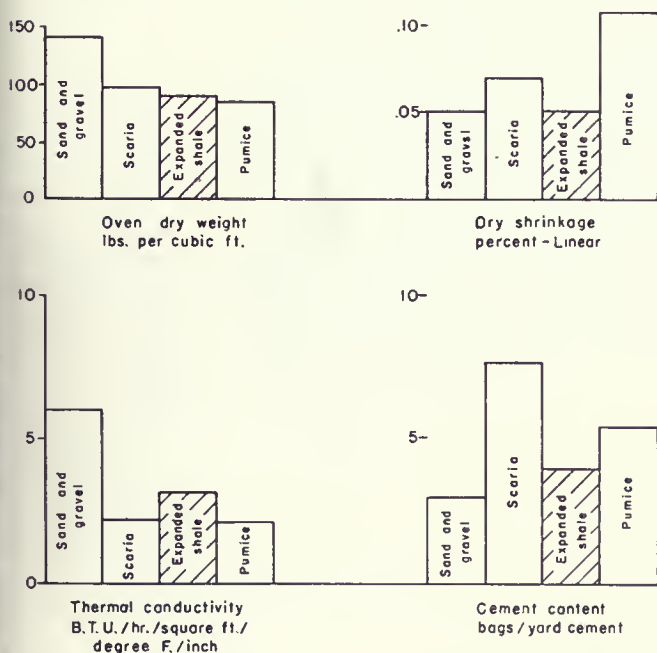


FIGURE 9. Physical properties of concrete made with natural lightweight aggregates, expanded shale, and sand and gravel.



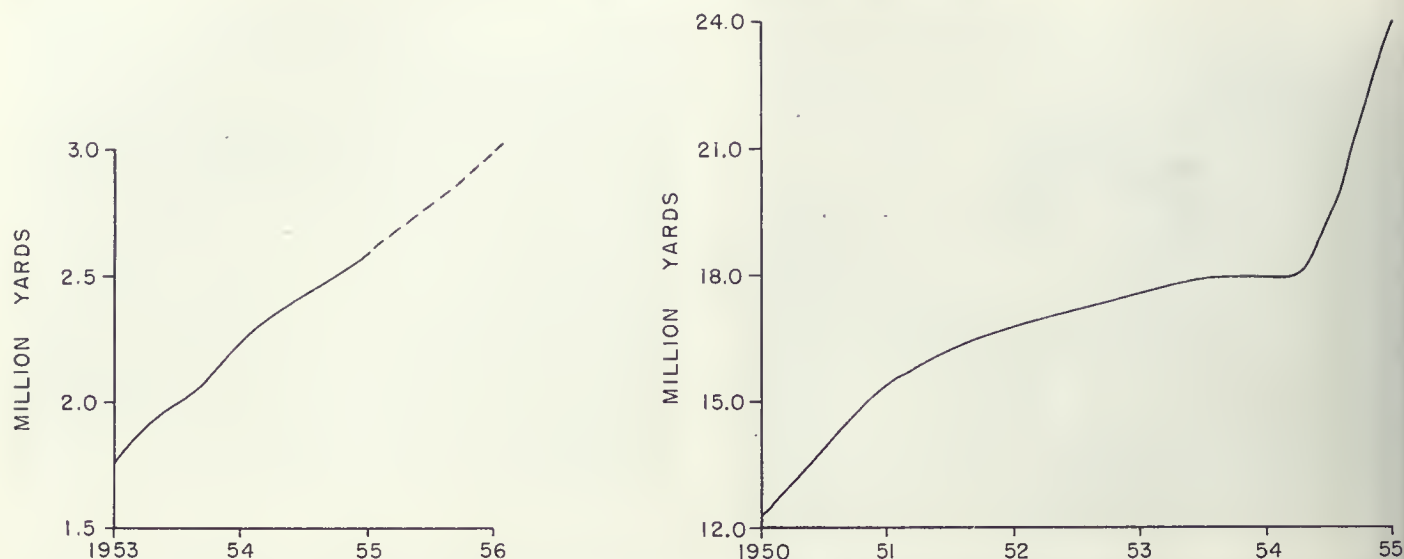


FIGURE 11. (Left) Expanded shale production in the United States. (Right) Lightweight aggregate production in the United States. (Pit and Quarry, January issues, 1951-56.)

and concrete made from it has better thermal and acoustical insulating properties than ordinary concrete.

On the other hand, most lightweight aggregate concrete has higher water absorption and curing shrinkage than ordinary concrete, and requires more cement to produce a given compressive strength than does sand and gravel concrete. Furthermore, most lightweight aggregates produce concrete with a 28-day compressive strength of less than 3,000 psi. Expanded and burned shales, however, are lightweight and yet produce concrete with compressive strength, water absorption, and curing shrinkage values more nearly comparable with those of sand and gravel concrete.

As the expansion of shale requires expensive equipment and fuel, it generally is more expensive to produce than natural lightweight aggregates such as pumice and scoria, which need only be crushed and graded after they are mined. Perlite and vermiculite are also processed by a heat treatment, but they have special uses and generally are not competitive with expanded shale. The high cost of production of expanded shale is partly offset by the general abundance of raw material sources and nearness to market areas.

**Marketing.** The following factors must be considered before a shale deposit can be put into operation:

- (a) The shale must expand when heated to an economically feasible temperature; this temperature should probably be less

than 2300°F. The shale should have a wide temperature range of expansion without becoming sticky.

- (b) The expanded shale must meet the A.S.T.M. specifications, C331-53T, for lightweight aggregate. These specifications are as follows:

- (1) Grading of aggregate: Aggregate shall be graded from coarse to fine within the limits shown in table 1.

- (2) Unit weight requirements:

Size designation	Dry loose weight lb. per cu. ft.
Fine aggregate	70
Coarse aggregate	55
Combined fine and coarse aggregates	65

- (3) The aggregate should also be free of any deleterious substances, i.e., organic impurities and unburned materials (not to exceed 2 percent dry weight), that might react with cement to cause spalling or other structural failures.
- (4) Drying shrinkage should not exceed 0.10 percent, and the surface of the concrete should show no popouts.
- (c) The deposit should be at least large enough to support an operation long enough to amortize the cost of the processing plant. It should also be homogeneous and so located geologically and topographically to allow mechanized, open-pit mining operations.
- (d) To minimize hauling costs the deposit should be near to a possible processing plant site, and near to markets.

As all of the operators in California obtain shale from captive deposits close to the plants, they provide no ready market for crude expansible shale from an independently operated deposit.

Table 1. Screen analysis of graded aggregate. Percentage (by weight) passing sieves having square openings.

Size designation	¾-in.	½-in.	3/8-in.	No. 4	No. 8	No. 16	No. 50	No. 100
Fine aggregate No. 4 to 0	--	--	100	85-100	--	40-80	10-35	5-25
Coarse aggregate ½-in. to No. 4	100	90-100	40-80	0-20	0-10	--	--	--
3/8-in. to No. 8	--	100	80-100	5-40	0-20	--	--	--
Combined fine and coarse aggregate ½-in. to 0	100	95-100	--	50-80	--	--	5-20	2-15
3/8-in. to 0	--	100	90-100	65-90	35-65	--	10-25	5-15





FIGURE 12. Quarrying expansive shale at Basalt Rock Company's shale quarry near Lake Chabot, Solano County. The shale (Cretaceous in age) from this quarry is trucked to a processing plant located nearby and made into lightweight aggregate for all types of concrete structures.



In 1956, expanded shale aggregate in California was valued at about \$5.00 per yard f.o.b. plant. This price was about three times as high as ordinary sand and gravel aggregate and two to three times as high as pumice and volcanic cinder aggregate. The price of standard 8 by 8 by 16 inch building blocks made with expanded shale was about the same as the price of blocks made with pumice and cinders, and only slightly higher than the price of heavyweight concrete blocks.

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# SILVER

By RICHARD M. STEWART

Silver has been produced in quantity in California since the gold-rush days. Most of the state's silver, especially in recent years, has been recovered from base metal ores mined in Inyo County. Silver has been the principal valuable metal in deposits of only two major districts in California—Calico and Randsburg. Statistics covering the state's annual silver output were not gathered before 1880, but since then and through 1954, about 105 million ounces have been produced. This represents about 2.8 percent of the national production, including that from Alaska, for the same period. California's silver production was 1,047,480 ounces in 1953, and the annual production for the years 1949 through 1953 averaged 1,029,610 ounces (Maurer, 1954, p. 4). Owing to the shutdown of the state's principal lead-zinc mine at Darwin, Inyo County, the amount of silver produced in California dropped to about 309,000 ounces in 1954.

**Mineralogy.** The most abundant silver minerals of California are cerargyrite ( $\text{AgCl}$ ), also known as horn silver; and miargyrite ( $\text{AgSbS}_2$ ). Silver may substitute for copper in the mineral tetrahedrite ( $\text{Cu,Fe,Zn,Ag}_{12}(\text{Sb,As})_4\text{S}_{13}$ ). Freibergite, which is silver-bearing tetrahedrite, is common in many mines in California and was very important as the source of silver in several deposits. Most of the silver now produced in California is obtained from argentiferous galena and silver-bearing lead or zinc minerals in the oxidized zone of lead-zinc deposits.

Native silver occurs principally as a secondary mineral. It is widespread, but in most deposits is not as abundant as other silver-bearing minerals. Native silver rarely is pure, but contains admixtures of other elements, particularly gold and copper. Electrum, an alloy of gold and silver, contains from 18 to 36 percent silver. Although the silver content of most of the lode gold produced in the state has been relatively low, lode gold mines have yielded an appreciable part of the total amount of silver produced. Most placer gold carries a lower proportion of silver than does lode gold.

Silver minerals that are important in other areas include argentite ( $\text{Ag}_2\text{S}$ ); proustite ( $\text{Ag}_3\text{AsS}_3$ ), also known as light ruby silver; pyrargyrite ( $\text{Ag}_3\text{SbS}_3$ ), also known as dark ruby silver; and stromeyerite ( $\text{Ag,Cu}_2\text{S}$ ).

**Localities in California.** Mines in San Bernardino County have been the source of most of the silver produced in California, followed by mines in Inyo and Shasta Counties in that order. Other counties that have yielded silver valued in excess of one million dollars are Calaveras, Kern, Mono, Nevada, and Plumas.

The lead-zinc deposits in the Darwin and Tecopa districts of Inyo County have been the chief sources of silver in California in recent years. These deposits are described in the section on lead in this bulletin. The ore milled at the Darwin mines has averaged from 5 to 7 ounces of silver per ton. Some marginal grade mill ore has contained as little as 1 ounce per ton, and some high-grade shipping ore has contained 20 ounces of silver per ton. Shipping grade ore from the principal mines in the Tecopa district has averaged about 11 ounces of silver per ton. Published reports indicate that most of the ore

shipped from other lead-zinc deposits in Inyo County had silver-lead ratios ranging from 1 ounce: 1 percent to 1 ounce: 3 percent (Carlisle, et al., 1954, p. 42). A notable exception is the Lee Flat mine in Inyo County, ore shipments from which have had silver-lead ratios as high as 10 ounces: 1 percent.

Silver was the principal metal sought in the South Fork district in Shasta County. At the Chicago mine, the source of about a million dollars worth of silver, freibergite occurs with galena in quartz veins in granitic rocks. Most of the silver produced in Shasta County, however, was recovered from massive sulfide deposits that contained copper, zinc, and minor proportions of precious metals. These deposits are described in the sections on copper and zinc in this bulletin. The following data show the proportion of silver to copper and zinc in the ore from some of the more productive mines of this type.

	Calculated proportions		
	Ag	Cu	Zn
Iron Mountain (Kinkel and Albers, 1951, p. 8) —	1	7.5	2.65
Shasta King (Kinkel and Hall, 1951, p. 3) —	1	2.9	8.7
Mammoth (Kinkel and Hall, 1952, p. 6) —	1	0.7	0.8
Afterthought (Albers, 1953, p. 13) —	1	0.5	3.2

The Iron Mountain mine was first worked to recover the silver contained in the gossan that capped the sulfide ore.

San Bernardino County has a total silver output valued at nearly 30 million dollars. Although some of this silver has been obtained from base-metal or gold mines, most of it was obtained from mines in which it was the principal metal. The most productive mines were those of the Calico district and the Kelly (California Rand) silver mine of the Randsburg district.

Rich silver ore was discovered in the Calico district (Wright, et al., 1953, pp. 125-133) in 1881, and the most productive mines were active from 1882 to 1896. The value of the total production of silver from mines in this district has been estimated variously at 13 million to 20 million dollars (Wright, et al., 1953, p. 126).

The Calico Mountains consist essentially of a Tertiary sequence, composed of volcanic rocks and lake deposits, which rests upon a pre-Tertiary crystalline basement. The Tertiary rocks are broadly divisible into three units. The lower two consist of sedimentary and volcanic rocks of Miocene age. Pliocene (?) andesite, the upper of these Tertiary divisions, rests unconformably on the Miocene units. The silver deposits were associated with tensional faults in the Miocene rocks and lie along a zone 5 miles long and 2 miles wide. The deposits may be classified as: (1) veins within or near prominent faults or fractures, and (2) shallow, pocketly disseminations.

The mined ore was chiefly cerargyrite (silver chloride) and embolite (silver chloro-bromide) in a gangue of barite and jasperoid silica. Most of the cerargyrite and embolite occurred as thin coatings in cracks, but thick lenses of nearly solid cerargyrite were not uncommon. Base metal minerals, manganese oxides and pyrite were present in minor proportions along with traces of gold;



some native silver was found. Barite formed as much as 95 percent of the vein material.

The Calico ores averaged 10 to 26 ounces of silver per ton, but some ores had values as high as \$2,000 per ton (DeLeen, 1950). At the price prevailing in 1894 of \$1.13 per ounce, this value would have represented ore containing about 1770 ounces of silver per ton. Although the veins persisted in the deepest workings, 550 feet, the ore shoots were shallow, and few mines exceeded a depth of 200 feet. Lateral workings were extensive in the larger mines, such as the Silver King, Odessa, and Garfield-Thunderer.

The Kelly (California Rand) silver mine (Wright, et al., 1953, pp. 133-138) was discovered in 1919, and has the largest silver output of any single mine in California—a recorded output valued at about \$16,000,000. The Kelly, a few bordering properties that also contained shipping-grade silver ore, and numerous silver prospects lie within a northeastward-trending area about 2 miles long and  $1\frac{1}{4}$  miles wide. The Kelly workings are confined to a zone 4500 feet long and 1200 to 1800 feet wide. Virtually all the known silver deposits of commercial interest are in the Rand schist, a pre-Cambrian formation that lies in the central western part of the area above. Pliocene continental sedimentary rocks and acidic volcanic intrusive rocks are exposed north and east of the Rand schist, and bodies of Mesozoic quartz monzonite have intruded the Rand schist in the northern and southern parts of the area.

The ore bodies are contained in well-defined veins that are broadly divisible into two sets; one set strikes about N. 40° E.; the other, and later, set strikes northward to north-northwestward. Dips flatten from 70° near the surface to 40° at depths exceeding 800 feet. Most of the veins terminate upward against a pre-mineral fault known locally as the "mud wall."

The veins of the northeastward-trending set are the most extensive; the Footwall vein has an exposed length exceeding 3500 feet and ranges in width from 40 to 80 feet. Six parallel veins, including the Shaft vein and Antimony vein, lie within a distance of 1400 feet to the southeast. The veins of the north-trending set are generally shorter, spaced at intervals of 200 to 500 feet, and range in thickness from 5 to 10 feet. Sixteen of these have been named, the more famous being the Harrel and Nosser veins.

Ore shoots in the veins are lenticular to pipelike in shape, from a few inches to 60 feet wide, and as long as 300 feet. Although the north-trending veins are not as extensive, in general they contain the best ore, and ore shoots are richest at intersections of veins of the two sets. Workings in the intersections of the Harrel-Antimony and Harrel-Shaft veins alone have yielded ore valued at \$12,000,000.

Miargyrite, freibergite and cerargyrite are the principal silver minerals; proustite and pyrargyrite are present in minor proportions. The vein gangue is composed mostly of fine-grained quartz and chalcodony. Pyrite and arsenopyrite are abundant in the northeastward-trending veins, much less so in the others. Chalcopyrite and native gold are rare.

Much of the ore mined was of very high grade. The richest probably assayed as high as 13,000 ounces of silver per ton (Hulin, 1925, p. 115). The range in grade

for most of the ore mined was 10 to 300 ounces of silver per ton, and the average approximated 50 ounces of silver and \$3.00 of gold per ton (Hulin, 1925, p. 99).

The mine has been worked mainly through 3 shafts, the deepest being 1660 feet. Level workings, mostly at 100-foot intervals and variously connecting the shafts, total more than 9 miles in length.

Two smaller districts, the Panamint City in Inyo County, and the Blind Spring Hill in Mono County, were mined principally for silver. The Panamint City district (Sampson, 1932, pp. 359-364) was most active in the 1870's. Here freibergite-bearing ore, valued at about \$2,000,000 was removed from quartz veins in limestone. The workings are shallow and most of them are appended to adits driven into hill slopes.

The Blind Spring Hill district, most active from 1862 to the early 1880's, is credited with a production valued at \$4,000,000 to \$6,000,000 in silver. The deposits here are notable in that stromeyerite ( $\text{Ag,Cu}_2\text{S}$ ), an uncommon mineral elsewhere, was the principal silver mineral. All the deposits were richest in the zone of oxidation and enrichment near the surface, and none was worked to a depth of more than 1100 feet (Ransome, 1940, p. 162).

The Mojave district in Kern County, although of interest chiefly for the gold content of its ores, has been the source of considerable amounts of silver. The gold and silver here occur in epithermal quartz veins related to Middle and Upper Tertiary intrusive volcanic rocks (Gardner, 1954, p. 52). Some of the silver was present as electrum, but cerargyrite and argentite were present in major proportions in some ore shoots (Tucker, 1935, p. 468). The cerargyrite was found to be very finely disseminated through the quartz above the water level, whereas argentite was the principal ore mineral at deeper levels. About 40 percent of the total value of the ore was represented by silver (Tucker, 1949, p. 221). The Cactus mine at Middle Buttes was the main source of silver in California during 1938 and 1939 (Gardner, 1954, p. 51).

Cerargyrite is the chief silver mineral in the deposits at the Annex (Silver Hills) mine in San Bernardino County. Native silver and silver sulfides contained most of the silver in the ore at the Waterman mine in San Bernardino County just west of the Calico district. Cerargyrite was abundant near the surface in this deposit.

*Mining Methods.* As most of California's silver output is derived from base metal ores, the mining operations for these ores are described in the sections on copper, lead and zinc in this bulletin.

Mining methods in the Calico district, San Bernardino County, most active from 1882 to 1896, are incompletely described, but much of the ore was recovered from large open stopes connected by unsystematic level workings. To quote Storms (1893, p. 344), "The policy which was pursued in those 'palmy days'—to gouge out the rich ore whenever it could be found, without regard to future condition of the mine—left most of the mines in very bad shape." And in referring to the Odessa mine, "In this mine are stopes from which thousands of tons of ore have been mined, and there is not a stick of timber of any kind in them . . . What applies to the Odessa in this respect is true to a great extent of every other large mine in Calico."



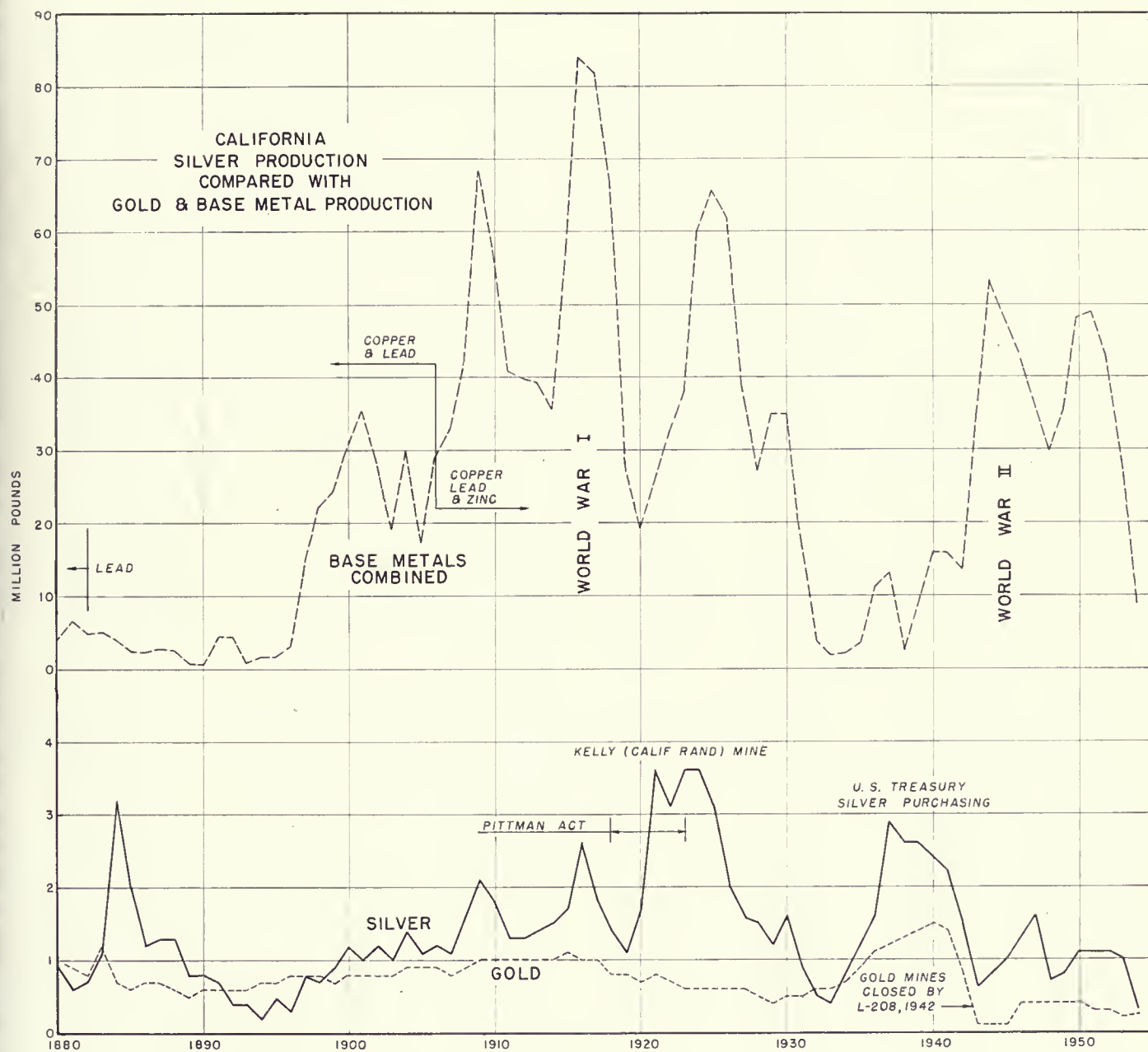


FIGURE 1.

In the Calico district, as well as in other early operations, the term "chlorider" was applied to one who, upon leasing a portion of a mining claim, mines only the high-grade ore (silver chloride) and does no development work. Nevertheless, the deposits were explored extensively, and not all the mines were developed unsystematically. The Silver King mine (Wright, et al., 1953, pp. 129-130), one of the first and most productive in the district, was originally worked through a 500-foot inclined shaft. Workings on the 4th, 6th, 7th, 8th and 9th levels connected to the adjacent Oriental mine. In operations after 1926, two vertical shafts were sunk 550 feet part to depths of 340 and 530 feet and level workings were extended to a total of at least 12,000 feet.

Ore from the Kelly (California Rand) mine in the Randsburg district was first removed from a glory hole.

Owing to the irregularity of the bodies that contained high-grade ore, subsequent development work was governed by the desire to follow the ore closely. Level workings from the main shaft were driven at 50-foot intervals down to the seventh level and mostly at 100-foot intervals below. The greatest depth attained was 1660 feet. The ground stood well and most stopes were open. Some shrinkage stopes were used, primarily to "provide a reserve of broken ore from which to draw if all the faces happen to 'pinch' coincidentally" (Parsons, 1921, p. 859).

*History of Production.* The production of silver in California was not separately recorded until 1880. The earliest mention of silver mining refers to the Alisal Ranch, Monterey County. Prior to 1825 an adit and



winze were supposedly driven here by three Chileans under the direction of Spanish padres. The ore was galena, thought to be argentiferous (Laizure, 1925, pp. 23 and 56).

Since 1849, by-product silver produced from the gold mines has been quite important. With mining interest concentrated on gold, little attention was paid to silver. However, in 1856 silver ore in the form of silver-bearing tetrahedrite with galena was discovered in the South Fork mining district of Shasta County (Tucker, 1923, p. 313). The Chicago mine, not located until 1866, was the largest source and is credited with production valued at about \$1,000,000. At first the ore was shipped to Swansea, Wales, for reduction.

The silver boom of the Comstock Lode in Nevada, in 1859 and 1860, finally led to the prospecting for silver in Alpine, Mono, and Inyo Counties, starting in the summer of 1861. The earliest silver mining in Alpine County (Logan, 1922, pp. 355-366) was not very successful, largely because the sulfide ores were not amenable to the ordinary free-milling processes. Later, Frue vanner concentrators were brought to the Colorado No. 2, the largest producer, and the concentrates were successfully chlorinated, with high recovery of gold and silver.

Silver-bearing ore was discovered on Blind Spring Hill, Mono County, in 1862. The district, quite active until 1890, is credited with a production valued at more than \$4,000,000.

Farther south, in Inyo County, the Cerro Gordo district was discovered between 1862 and 1866; the Darwin district was discovered in the early seventies.

The Calico district, San Bernardino County, was active mainly from 1882-96, but was worked after that date.

In 1919, the California Rand silver mine was discovered. For several years its annual production had the highest value of any silver mine then operating in the United States. It was operated by various companies until it was shut down in 1942. The mine was reopened in 1946, but operations there have been mostly of an exploratory nature. It has contributed more than half of the recorded silver production from San Bernardino County.

The Pittman Act (Dunlop, 1921, p. 740) was of importance to silver producers during the period April 1918 to June 1923. Under this act 350,000,000 silver dollars were made available for melting. The silver thus obtained was used by the United States and the Allied Nations to settle trade balances in India, China, and other large silver-using countries. New domestic silver was purchased by the Mint at a guaranteed minimum price of approximately \$1.00 per ounce. In June of 1923, the Treasury Department ruled that enough fine silver had been purchased under the Act. Altogether 208,622,057 fine ounces were obtained for export by melting of the dollars, but only 200,585,035 fine ounces of new domestic silver were purchased by the Mint (Dunlop, 1925, pp. 599-600).

Since 1933, the government policy of purchasing all newly mined domestic silver has been the most important economic factor in the silver mining industry.

*Utilization.* Silver has been used by man for thousands of years. The malleability and ductility of the

native metal allowed it to be shaped even with the crudest of tools. Owing to its relative scarcity and its chemical stability under normal conditions, its dominant use from earliest times has been as a measure of wealth and as a medium of exchange.

Use of silver in coins is not as great today as it once was. In recent years only the subsidiary coins, half-dollars, quarters and dimes, have been minted in the United States. The intrinsic value of silver coins depends upon the weight and fineness of the coinage alloy (fineness being the proportion of pure silver expressed in parts per thousand), and the monetary value may be greater or less. The principal alloys used in coinage are binary silver-copper alloys, the copper providing greater resistance to wear. The fineness of coinage alloys in most countries ranges from 500 to 900, although some coins in circulation in Mexico have a fineness of only 300 (Leach, 1953, p. 381). The standard fineness of United States silver coins is 900. The weight in grams of these coins is as follows: dollar, 26.73; half-dollar, 12.5; quarter, 6.25; and dime, 2.5 (Director of the Mint, 1953, p. 62).

Second to its use as a monetary metal is the use of silver in the arts—silverware, both sterling and plated, and jewelry. The fineness range of the silver-copper alloys that are used for silverware is similar to that of the monetary alloys, but sterling silver which is 925 fine is the accepted standard for silverware in the United States and England. Much jewelry is manufactured of sterling silver, but some gold-silver alloys are also used. Silver hardens gold and lightens its color. A white-colored gold alloy results if 50 to 60 percent silver is added. A wide variety of yellow colors is obtained by adding copper, and the ternary gold-silver-copper alloys have a greater use in modern jewelry than the gold-silver alloys.

The use of silver in industry is a relatively recent development, but the proportion of silver thus used continues to rise. Some of the physical properties of silver that make it useful are: (1) high thermal and electrical conductivity (greater than copper, gold, or aluminum); and (2) a density of 10.49 intermediate between lead at 11.34 and copper at 8.96.

Silver, owing to its excellent qualities as a conductor of heat and electricity, was used extensively during World War II in place of copper. Large amounts of silver were loaned from the monetary stocks of the treasury to industry for use in such objects as bus bars. Silver also is used in other electrical contacts, commonly in silver-molybdenum or silver-tungsten mixtures prepared by powder metallurgy processes. A silver-copper alloy, identical to the monetary alloy, also is widely used for contact points. The conductivity of silver is utilized in electrical circuits imprinted with a silver flake paint. The development and expansion of the electrical and electronic industries undoubtedly will require increasing amounts of silver.

Silver solders and brazing alloys, generally termed "silver brazing alloys" (Leach, 1953, p. 390), have relatively low melting points and are highly resistant to corrosion. Metal parts may be soldered or brazed together with these alloys, and the resulting joint will have very high strength. Such alloys are especially useful in joining such components as fuel or oil lines on aircraft



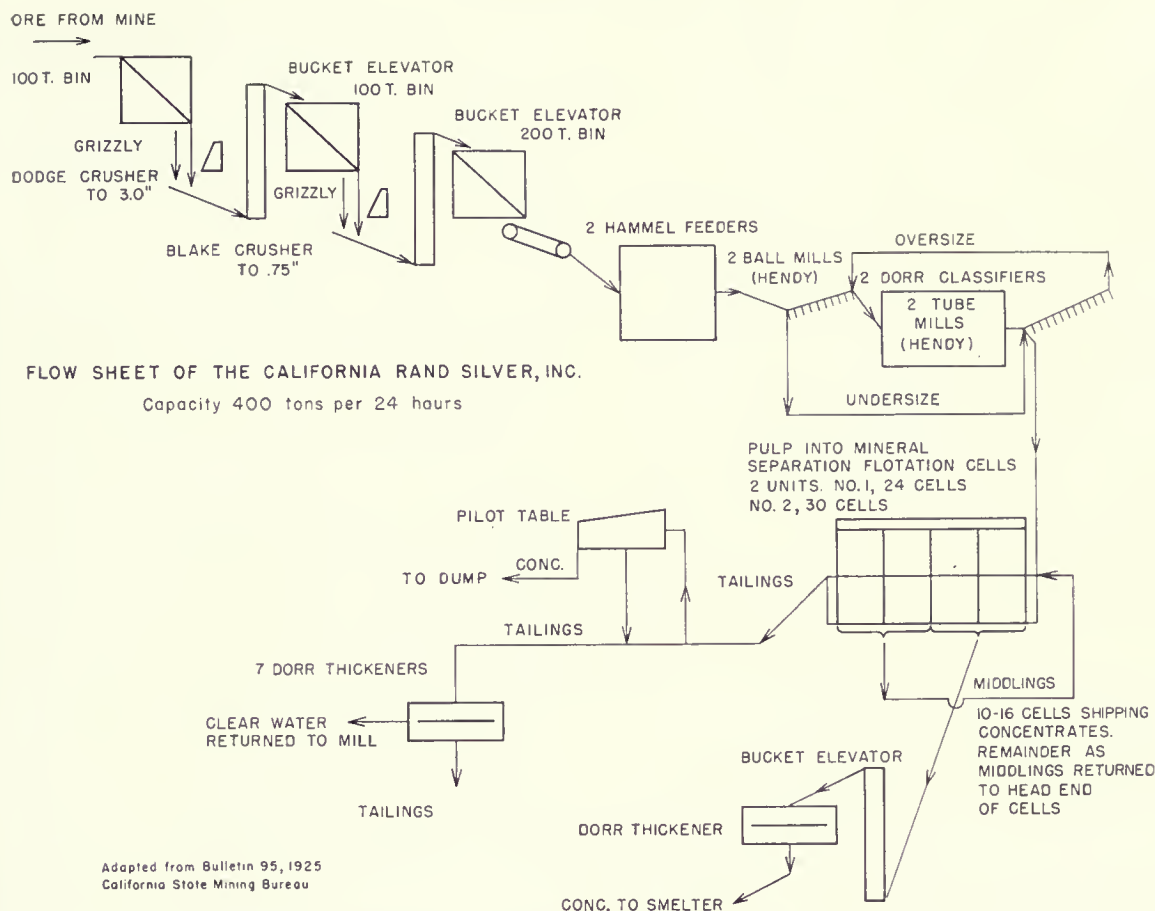


FIGURE 2. Flow sheet of mill at Kelly (California Rand) silver mine, San Bernardino County. (After Hulin, 1925, p. 120.)

wherein joint failures could be disastrous. Copper and zinc are the metals most commonly alloyed with silver in this application; cadmium, tin, nickel and manganese are also used.

The photographic industry consumes large amounts of silver each year in the form of silver nitrates, and practically every field of human endeavor is touched upon by the photographic process.

The medical profession makes use of the antiseptic and corrosion resistance properties of silver as silver plates or silver leaf over surgical incisions. Silver amalgam, consisting of powdered silver, tin, copper and zinc, mixed to a proper consistency with mercury, is used extensively by the dental profession.

Silver is used in the manufacture of chemical and laboratory equipment because of its high resistance to corrosion. Owing to the high reflectivity of a polished silver surface, silver is particularly useful for backing glass for mirrors and for coating other metals for reflectors.

The effects of alloying small amounts of silver with other metals, particularly in the manufacture of bearing metals, are being studied. A large-scale research program, The American Silver Research Project sponsored by the principal silver producers and dealers, indicated that the greatest hopes for increasing the use of silver lie in the metallurgical field (Bell, 1955, p. 792).

The accompanying table (Handy and Harman, 1956, p. 30) shows the major domestic uses of silver for the period 1951-1955.

Consumption of Silver in Millions of Ounces.

	1951	1952	1953	1954	1955
Arts and industries .....	110.0	95.0	105.0	85.0	100.0
Coinage .....	44.4	57.3	42.8	53.1	8.2
Total .....	154.4	152.3	147.8	138.1	108.2

**Beneficiation and Extractive Metallurgy.** Silver generally has been recovered from ores whose silver contents lie within the range of a few ounces to a few thousand ounces per ton. As more and more complex precious metal ores were mined, the processes for recovering silver changed from simple amalgamation to leaching or smelting. Today, nearly all silver ores are treated by cyanidation or by smelting, and either process may be preceded by concentration.

The amalgamation process involves bringing finely divided ore into contact with mercury, either on an amalgamating plate or by introducing mercury into the grinding circuit. Silver becomes wetted and absorbed by the mercury to form a substance known as amalgam. Silver and mercury may be present in various proportions, as amalgam consists in part of silver-mercury alloys and in part of silver particles adhering to and coated by the mercury.



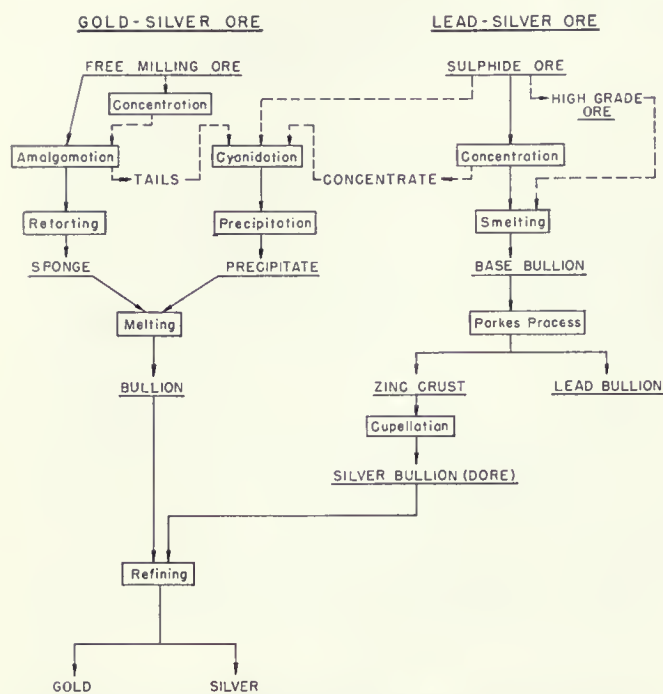


FIGURE 3. Schematic diagram showing beneficiation and extractive metallurgical processes for gold-silver and lead-silver ores.

As the amalgamation of more and more complex silver-bearing ores was attempted, the process was modified by the use of additional reagents, such as salt and copper sulfate, or by conducting the process in copper or iron pans and with the aid of external heat. It was found that precious-metal ores in which the silver was not present as silver chloride could be more effectively amalgamated if the silver was first converted to silver chloride by the use of a chlorine reagent. Eventually, this process evolved into a chloridizing roast. The resulting silver chloride then was either reacted upon to precipitate silver for amalgamation or dissolved by a brine or sodium thiosulphate solvent from which the silver was finally precipitated. The amalgam produced by any of the amalgamation processes must be further treated by retorting, the end products being a precious metal sponge and liquid mercury.

The cyanide leaching process, introduced around 1890, superseded all others and still is in use in some parts of the Americas. Cyanidation involves leaching finely ground ore with a weak aqueous solution of sodium or potassium cyanide. The precious metals contained in the ore are dissolved and recovered later by precipitation effected by zinc shavings, zinc dust, or carbon. The cyanide reactions are similar for both silver and gold, the principal differences being the rate of dissolution of the metals and the optimum strength of the cyanide solutions. Experiments with pure metals have shown that silver dissolves at about half the rate of gold and that the solution strength that results in maximum rates of dissolution is 0.05 percent NaCN for gold and 0.10 percent NaCN for silver (Barsky, 1935, pp. 670-672).

Silver minerals most amenable to cyanide treatment are argentite ( $\text{Ag}_2\text{S}$ ), native silver and the silver haloid minerals. Sulfarsenides and sulfantimonides of silver

and argentiferous galena and sphalerite are treated with greater difficulty; silver contained in manganese minerals can be recovered only by special treatment.

Flotation is the generally practiced method of concentration of silver-bearing ores, whether they are the precious metal or base metal type. Figure 2 shows the flotation practice at the mill of the Kelly (California Rand) silver mine in San Bernardino County (Hulin, 1925, p. 120).

Silver in base metal ores follows their processing through smelting, described in sections on copper, lead and zinc in this bulletin, and is ultimately recovered in the precious-metal sections at the smelters or refineries.

Beneficiation and extractive metallurgical processes for silver-bearing ores are schematically illustrated in figure 3.

**Silver Refining.** If the extraction of silver from precious metal ores is effected by cyanide treatment or amalgamation, the precipitate or sponge from the amalgam respectively must be melted to obtain a bullion. Such bullion contains both silver and gold and usually some base metals. A gold- and silver-bearing bullion, known as doré bullion, is a product resulting from the metallurgical treatment of precious metal or base metal ores at a smelter. The silver and gold from both types of bullions can be separated by a dry process, by acid parting, or by one of several electrolytic methods.

The dry process most commonly used, the Miller process, involves the conversion of silver to silver chloride in the molten bullion. Chlorine gas is introduced into molten bullion, and the resulting impure silver chloride is further refined to pure silver (Wagor, 1945, pp. 275-276). This method is restricted to the treatment of bullion containing relatively small proportions of silver. At the Homestake Mine, South Dakota, silver bullion is refined by this method and averages about 980 fine (Dorr, 1950, pp. 205-206).

Refining of silver by acid parting usually involves the use of sulfuric acid; nitric acid can be used but normally is more expensive. The process consists of several steps (Wagor, 1945, pp. 276-278): (1) blending bullion lots so that the proportion of silver to gold lies within the range of 2-1/4:1 to 4:1; (2) melting blended bullion and granulating or casting into thin slabs; (3) acid treatment in cast iron pots; (4) recovery of gold from residues; and (5) recovery of silver from the silver sulfate solution by precipitation, usually effected by copper replacement. The silver precipitate then is melted and cast into bars.

Electrolytic refining processes (Wagor, 1945, pp. 278-287) have supplanted acid parting systems at most refineries. Two processes, the Moebius and Balbach, are used for silver-predominant bullion, and the Wohlwill process is used for gold-predominant bullion. At the Selby, California, smelter of the American Smelting and Refining Company, the Moebius process is used to treat doré bullion, and the resultant sludge is treated by the Wohlwill process to recover the gold. In both the Moebius and Balbach processes, a bullion anode is subjected to electrolysis in an electrolyte composed of a weak solution of silver nitrate and containing excess nitric acid. Silver crystals are collected at the cathode, which in the Moebius system is a thin strip of pure silver and in the



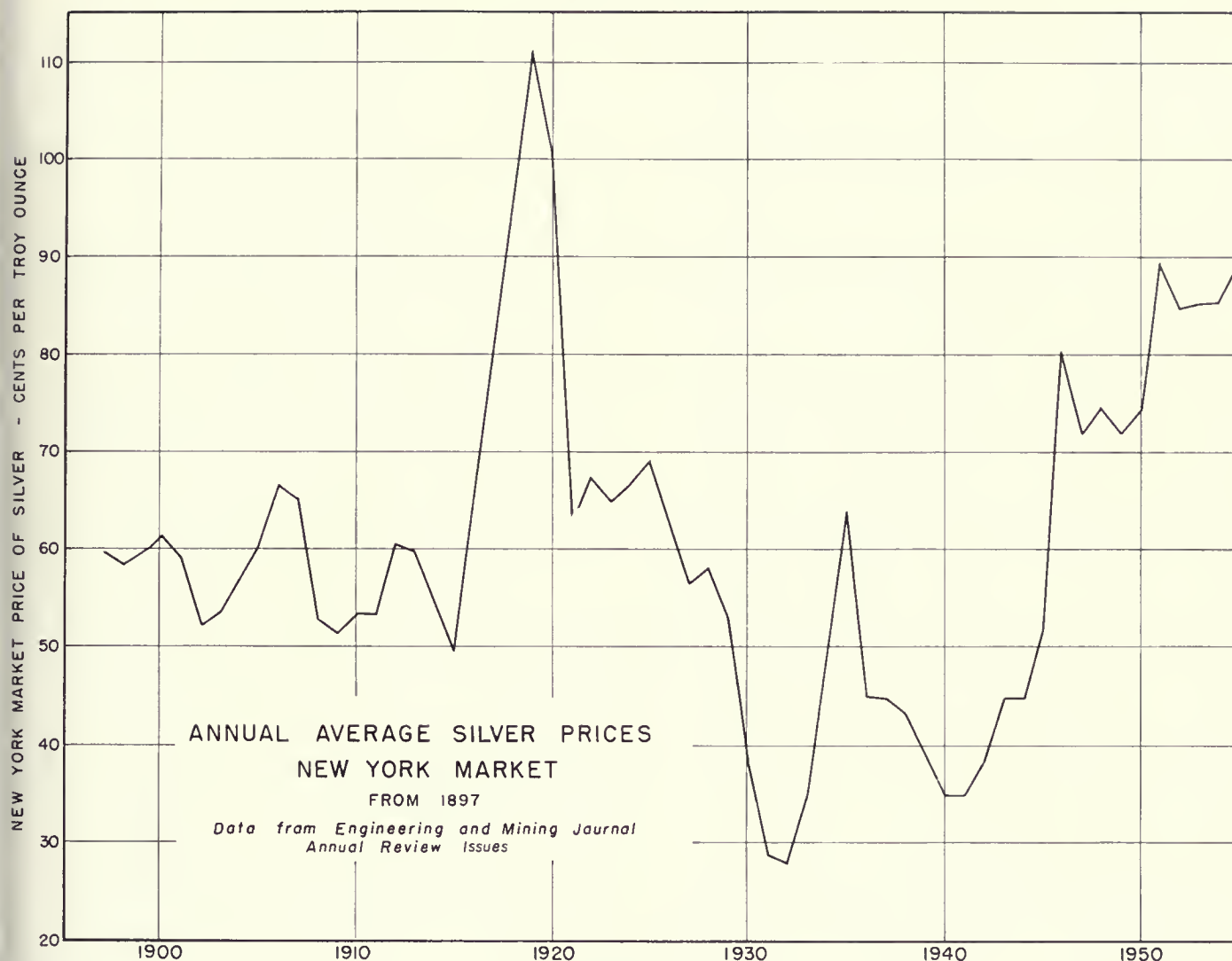


FIGURE 4.

Balbach system is a graphite plate. The two processes differ also in the positioning of the anodes and cathodes, in the cell construction, and method of collecting the silver crystals. Gold is left in a sludge and is treated separately.

Theoretically, fine silver would be 1000 fine, but the standard in this country is 999. Reputable refineries usually maintain a product of 999.2 to insure the acceptance of their silver (Leach, 1953, p. 380). Modern refining methods can produce such fine silver that copper is sometimes added to bring the fineness down to the accepted standard. The fineness of the silver is stamped upon each bar.

**Marketing.** International trade in silver is dominated by the regulations of the various governments. The Bank of Mexico has been a particularly powerful influence as it purchases and sells silver so as to stabilize the price as much as possible.

All domestically mined silver is purchased by the United States Treasury, mostly through smelters. Government purchase of newly mined domestic silver dur-

ing the past two decades was started by presidential proclamation in 1933 at a price of 64.4 cents per ounce, and continued at various prices until 1939, when the price was set at 71.11 cents. An act of July 31, 1946, set the price at 90.5 cents per ounce, and this act still governs the price of all newly mined domestic silver. Except for a period during World War II years, when much silver was channeled directly into industrial use, the Treasury has acquired all new silver in the United States.

Smelters will purchase ores and concentrates containing silver, but do not make payment for all of the silver contained. The smelter payment, which is normally based on the Treasury price, depends on the type of ore. In order for the smelter payment to be based upon the Treasury price for silver, the seller must execute an affidavit stating the date the silver-bearing ore was mined and the ownership of such ore. Payment for silver contained in precious and base-metal concentrates and ores is outlined in the accompanying table (Bramel, 1948, pp. 165-166, and open schedules from several smelters).



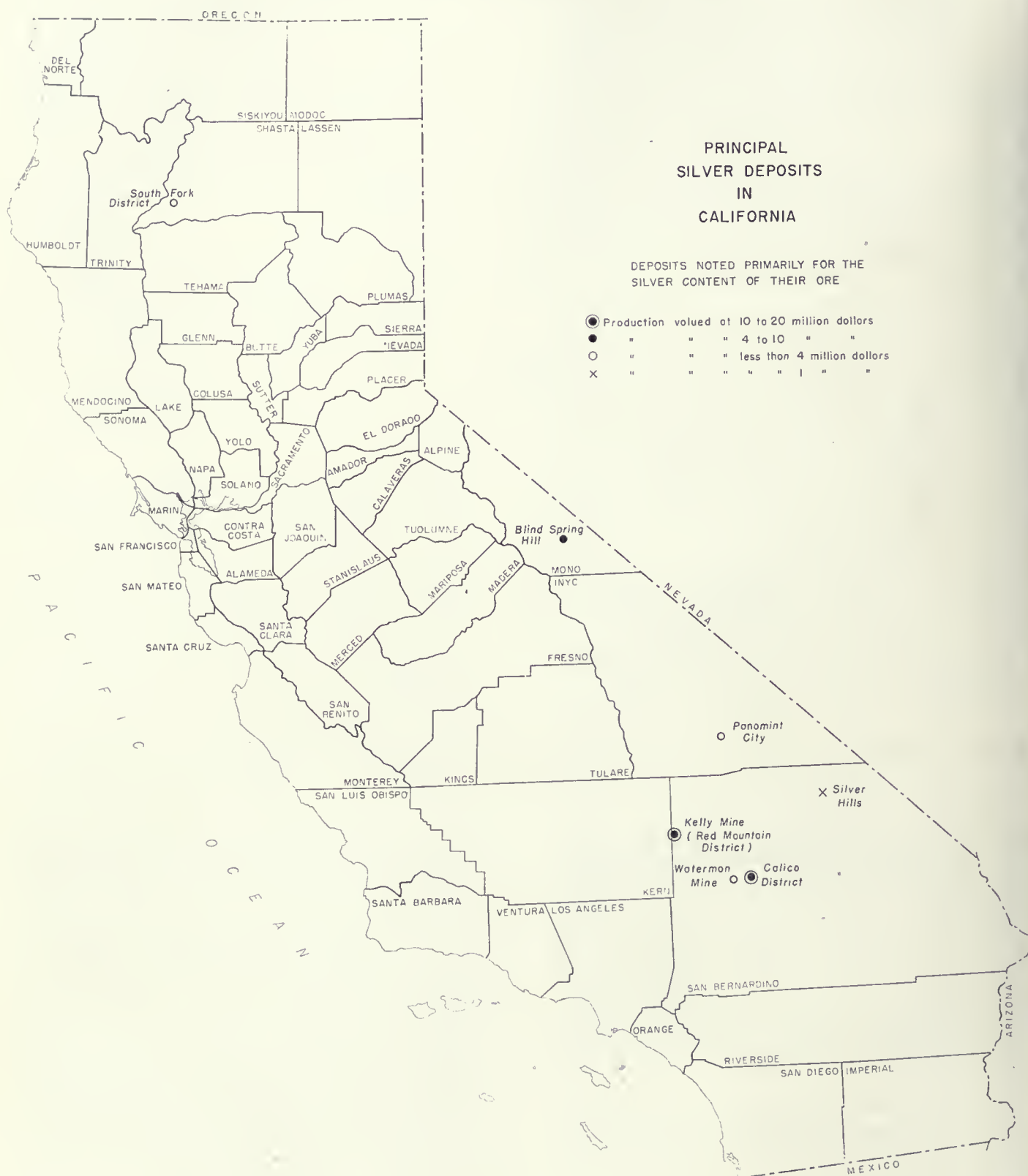


FIGURE 5.



*Payment for silver in precious and base-metal concentrates and ores.*

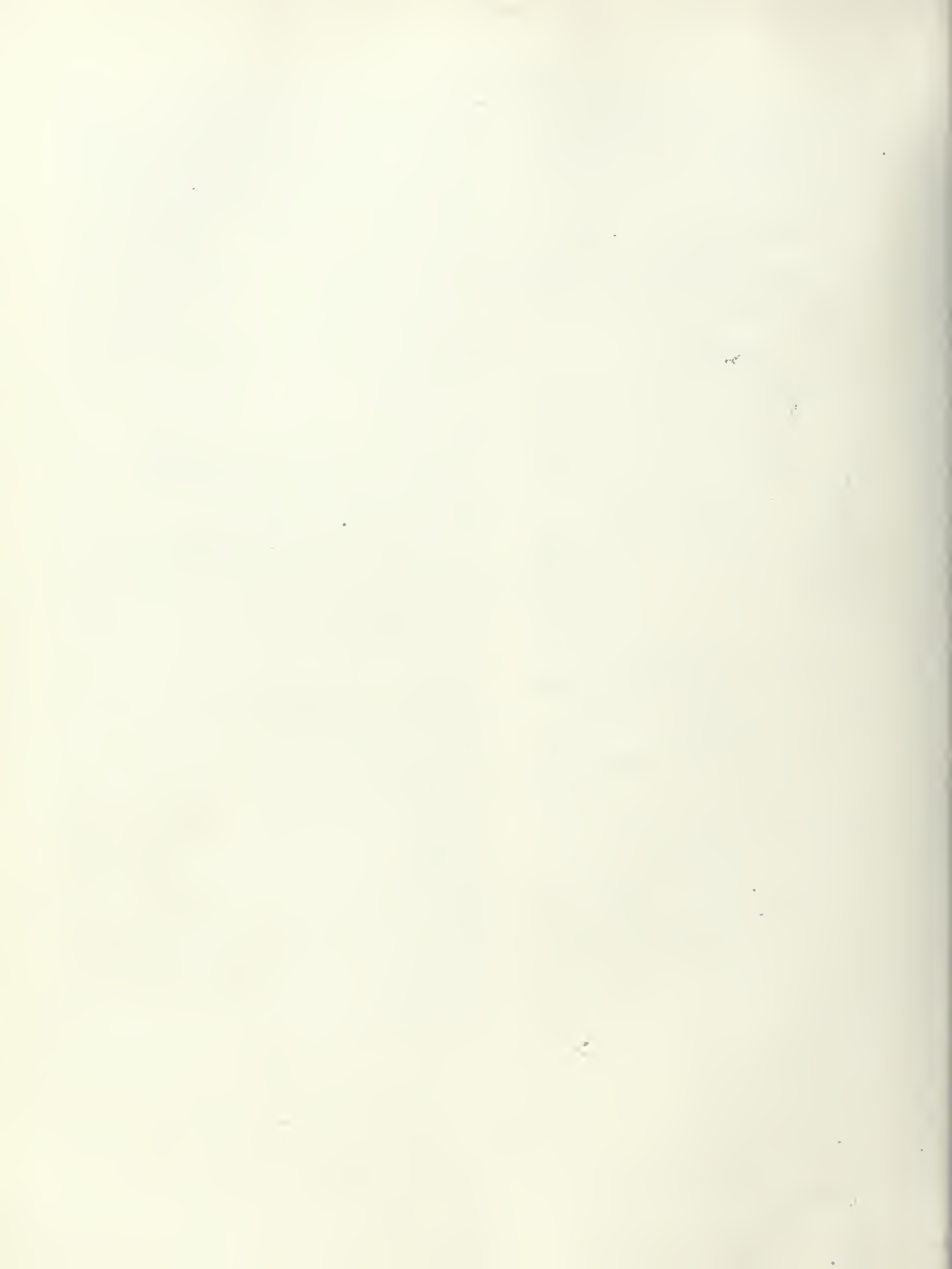
Type of ore	Percentage of silver paid for	Minimum amount of silver paid for
Gold and silver	95 (1 ounce per ton minimum deduction)	1 ounce
Copper	95	
Lead	95 (1 ounce per ton minimum deduction)	1 ounce
Zinc	80	1 ounce

During 1954 the New York price for foreign and secondary silver was constant at 85.25 cents per ounce. Figure 4 shows the trend of silver prices since 1897.

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## SODIUM CARBONATE

BY WILLIAM E. VER PLANCK

Approximately half of the natural sodium carbonate, commonly called soda ash, produced in the United States is obtained from California; the remainder comes from a single operation in Wyoming. Although natural sodium carbonate compounds comprise less than 10 percent of the sodium carbonate produced in the United States, west coast industries consume natural sodium carbonate almost exclusively. Most of the sodium carbonate produced in the United States is manufactured from common salt by the ammonia-soda or Solvay process, in which ammonia and salt are combined with carbon dioxide obtained by calcining limestone with coke. Ammonia-soda plants are ordinarily located near supplies of salt, coke, and limestones.

*Geology and Mineralogy.* Sodium carbonate is a very soluble salt that is found in the brines of certain springs and saline lakes and in deposits formed by the evaporation of sodium carbonate brines. Trona ( $\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$ ) is the most common sodium carbonate mineral. It is a very soluble, gray or yellowish, translucent mineral that occurs in fibrous or columnar masses or, less commonly, in cleavable plates. Natron ( $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ ) is a very soft mineral that readily dehydrates on exposure to dry air. Additional sodium carbonate minerals include thermonatrite ( $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ ), nahcolite ( $\text{NaHCO}_3$ ), burkeite ( $2\text{Na}_2\text{SO}_4 \cdot \text{Na}_2\text{CO}_3$ ), and hanksite ( $9\text{Na}_2\text{SO}_4 \cdot 2\text{Na}_2\text{CO}_3 \cdot \text{KCl}$ ).

The only deposit of sodium carbonate minerals that is being worked in the United States is near Green River, Wyoming. Although sodium carbonate brines have long been known in that area and were worked for sodium carbonate prior to World War I, sodium carbonate minerals were first encountered in 1938 in a test well drilled for oil. In the discovery well saline minerals occur in the 630 foot interval between 1190 feet and 1820 feet. They include trona, northupite ( $\text{MgCO}_3 \cdot \text{Na}_2\text{CO}_3 \cdot \text{NaCl}$ ), pirsomite ( $\text{Na}_2\text{CO}_3 \cdot \text{CaCO}_3 \cdot 2\text{H}_2\text{O}$ ), gaylussite ( $\text{Na}_2\text{CO}_3 \cdot \text{CaCO}_3 \cdot 5\text{H}_2\text{O}$ ), and two additional minerals, shortite ( $\text{Na}_2\text{CO}_3 \cdot \text{CaCO}_3$ ) and bradleyite ( $\text{Na}_2\text{PO}_4 \cdot \text{MgCO}_3$ ), that were first found here (Smith, 1942). The saline minerals occur for the most part as crystals disseminated in clay near the base of the Green River (Eocene) formation. A section about 10 feet thick, however, is composed of trona that is notably free from traces of chloride and sulfate and contains only about 5 percent of insoluble matter. Further test drilling revealed that massive trona forms a flat to gently dipping bed at a depth of about 1500 feet beneath a 30 square mile area.

*Localities in California.* All of the sodium carbonate produced in California is obtained by three plants from the brines of Searles Lake and Owens Lake. These localities and the methods of recovery are described in the general section on salines in this bulletin. As mentioned in that section, Searles Lake contains two porous, brine saturated crystal bodies, the upper and larger of which is approximately 71 feet thick, and the lower, 35 feet thick. The upper brine contains 4.80 percent sodium carbonate and the lower brine, 6.78 sodium carbonate. Owens Lake contains a crystal body similar to those of

Searles Lake except that its maximum thickness is 9 feet and the sodium carbonate content of the brine ranges from 11.98 percent in winter to 16.62 percent in summer.

The brines of Mono Lake, Mono County, and Borax Lake, Lake County, also contain sodium carbonate and deposit trona upon evaporation. Mono Lake is comparatively distant from markets, and its brine is far below saturation. The climate is not favorable for solar evaporation. The small Borax Lake, which has an area of only 200-300 acres, is estimated to contain a maximum of 23,000 tons of sodium carbonate (Averill, 1947).

Workable bodies of sodium carbonate minerals have not been found in California. The crystal bodies of Searles Lake and Owens Lake consist of intimate mixtures of salts such as trona, hanksite, halite, and borax that cannot be profitably mined at present, but may be potential reserves. Efflorescent crusts containing trona and thermonatrite occur in Death Valley and on the margins of many playas. One of the largest deposits of this type in California is the trona reef along the east side of Searles Lake, for which the town of Trona was named. An analysis (Gale, H. S., 1915, p. 294) shows that the reef is composed of insoluble matter and soluble salts and contains less than 50 percent trona. Deposits of this type are too small and too low in sodium carbonate to be of present economic interest. About 1908, a company attempted to produce crude alkali from this material but did not get into production.

*Methods of Recovery.* Nearly all sodium carbonate brines are complex and contain relatively high proportions of bicarbonate, sulfate, chloride, and borate. Therefore, the recovery of marketable sodium carbonate from them is comparatively difficult. Under favorable circumstances solar evaporation is applicable to unsaturated brines, and on Owens Lake trona contaminated with several percent of insoluble matter, chloride, and sulfate was recovered from the late 1880's to 1921. The trona was calcined to yield soda ash about 95 percent pure. The evaporation of saturated brines such as the present Owens Lake brine and Searles Lake brine yields complex salts that cannot be easily separated. The American Potash & Chemical Corporation, however, evaporates the upper brine of Searles Lake in vacuum pans and obtains a concentrated liquor from which potash and borax are obtained. Sodium chloride and the double salt burkeite ( $2\text{Na}_2\text{SO}_4 \cdot \text{Na}_2\text{CO}_3$ ) crystallize in the evaporators and are removed as solids. Further treatment of the burkeite yields sodium sulfate and soda ash 99½ percent or more pure. This soda ash is a granular product having a bulk density of 60 pounds per cubic foot that is called dense ash.

The chilling of a sodium carbonate brine results in the crystallization of natron ( $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ ) which can be dehydrated to soda ash. If sulfate is present, however, the natron is likely to be contaminated with mirabilite ( $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ ), with which it crystallizes isomorphously.

Carbonation is another process used to recover sodium carbonate from brines. Carbon dioxide is bubbled through



brine-filled towers, and a comparatively insoluble sodium carbonate compound crystallizes. With brines that contain less than about 9 percent sodium carbonate, sodium bicarbonate forms; but with brines rich in sodium carbonate such as that of Owens Lake, sodium sesquicarbonate (trona) forms. The crystals of bicarbonate or sesquicarbonate are then calcined to produce soda ash. The carbonation process is, in many respects, like the ammonia-soda or Solvay process in which ammonia gas is dissolved in sodium chloride brine, and the ammoniated brine is carbonated to yield sodium bicarbonate. Carbonation must be carefully carried out to produce uncontaminated crystals coarse enough for efficient separation from the mother liquor. The calcination of precipitated bicarbonate or sesquicarbonate yields light soda ash, a fluffy material having a bulk density of 35 pounds per cubic foot or less and with a high proportion of its particles in the minus 100 mesh range. Dense ash of 50-65 pounds per cubic foot density is prepared by adding enough water to the light ash to produce the monohydrate ( $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ ). An agglomerated soda ash results from the drying of the monohydrate and the removal of its water of crystallization.

At Searles Lake the American Potash & Chemical Corporation carbonates the lower brine, whereas the West End Chemical Company Division of Stauffer Chemical Company carbonates a mixture of the upper and lower brines. Both plants obtain sodium bicarbonate from the carbonating towers. The light ash obtained by calcining the bicarbonate is not marketable, but washing and drying steps change it to dense ash more than 99½ percent pure. At Owens Lake the Pittsburgh Plate Glass Company, Columbia Chemical Division, operates a comparatively small carbonation plant. The carbonation of the brine results in the formation of sodium sesquicarbonate which is either dried and marketed or calcined to light ash.

The trona deposit near Green River, Wyoming, is owned by the Intermountain Chemical Corporation, a joint subsidiary of Food Machinery and Chemical Corporation and National Distillers Products Corporation (Chem. Eng., 1953; Romano, 1952). A plant of 300,000 tons per year design capacity was completed in 1953 at a cost of \$20 million. This cost included \$2 million spent for exploration, the perfection of a low cost mining method, and the development of a refining process. Trona is mined at the rate of 2,500 tons a day by methods and equipment similar to those employed for mining coal. The crude trona is first refined by dissolving it in water and recycled mother liquor, clarifying the solution with thickeners followed by filtration, and reprecipitating trona (sodium sesquicarbonate) by evaporation. The sodium sesquicarbonate is then converted to light ash in a rotary calciner, and facilities have been installed to change a portion of the light ash to dense ash.

*Uses.* Soda ash is one of the most useful alkali materials, and it is consumed in greater quantity than any other industrial chemical except salt and sulfuric acid. In addition, it is usually used in the preparation of other sodium compounds because it is comparatively cheap and reacts readily with most other chemicals. For some uses, caustic soda ( $\text{NaOH}$ ) is a substitute for soda ash, particularly if the consumer purchases soda ash and causti-

cizes it before use; but for many purposes soda ash has no substitute.

The largest use for soda ash in California is in the manufacture of glass, and the estimated consumption for this purpose is in the order of 150,000 to 200,000 tons a year. Probably the next largest use is in soap and cleansers; and smaller amounts are consumed in petroleum refining, water softening, the treatment of certain ores, and in the manufacture of chemicals such as sodium phosphates, sodium nitrate, sodium silicate, sodium bicarbonate, and washing soda ( $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ ). Uses that require significant amounts outside of California include the preparation of alumina for reduction to aluminum, the soda pulp process of preparing pulp from hardwood, the manufacture for sale of caustic soda by the lime-soda process, and the production of sodium sesquicarbonate. In California this compound is recovered directly from brine at Owens Lake.

Common glass is composed of 69 to 72 percent  $\text{SiO}_2$  obtained from silica sand, 13-15 percent  $\text{Na}_2\text{O}$  obtained from soda ash, 12½-13½ percent  $\text{CaO}$  obtained from limestone, and smaller amounts of several other oxides. Pure silica has such a high melting point and such a high viscosity that it cannot be made into glass by ordinary methods. When soda ash and limestone are fused with silica, the carbonates lose their carbon dioxide; and the sodium oxide and calcium oxide, combining with the silica, form a glass with reduced melting point and viscosity that can be fashioned into useful articles. Glass that contains only silica and sodium oxide is water soluble. Although it has no value as commercial glass, it is commonly crushed and dissolved to yield sodium silicate solutions for a host of purposes. Both the glass and sodium silicate industries specify dense soda ash. In the glass industry, uniformity in all raw materials is insisted upon because even slight changes result in non-uniform glass that cannot be handled in automatic fabricating machines.

In the soap and cleanser industry soda ash and modified sodas (sodium bicarbonate and sodium sesquicarbonate) are added to powdered soap to provide a specified alkalinity. Some soap is made by neutralizing fatty acids with soda ash, but most soap is produced by the saponification of fats and oils with caustic soda. The large quantity of caustic soda consumed formerly was obtained by causticizing soda ash at the soap plant, but present practice is to purchase caustic soda. In petroleum refining, products treated with sulfuric acid are neutralized with dilute caustic soda prepared from soda ash. In water softening, soda ash with lime hydrate is used to precipitate calcium and magnesium compounds.

*Markets and Price.* Except for small quantities, which are handled through chemical supply houses, all sales of soda ash are made by producers' salesmen directly to the consumers. Because soda ash is a comparatively inexpensive commodity, freight charges comprise a significant part of the price that the consumer pays. Surrounding every producer is an area within which he can deliver his product for less than it can be obtained from another producer at a different locality. The area within which the delivered price of soda ash produced in California is less than that of soda ash produced by eastern ammonia-soda plants is confined to the West Coast, and its eastern limit lies west of Salt Lake City. Since Wyoming soda



ash was placed on the market, sales of California soda ash have declined. Wyoming ash is competitive in the northwestern states, and it is also used in California by plants whose owners have a financial interest in the Wyoming operation. California producers expect, however, that the continued growth of industrial development in the West will gradually restore the markets that have been lost.

In 1955, dense soda ash sold for \$35 per ton f. o. b. California plants, in bags, carlots.

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## SODIUM SULFATE

BY WILLIAM E. VER PLANCK

California contributes 80 to 90 percent of the sodium sulfate produced from natural sources in the United States. Only a quarter of the national production, however, was derived from natural sources. Sodium sulfate is a by-product of several chemical processes, and additional amounts are imported into the United States, principally from western Canada. The California production comes from Searles Lake, San Bernardino County.

**Geologic Occurrence and Mineralogy.** Natural sodium sulfate occurs in the brines, crystal bodies, and efflorescent crusts of playa lakes and as beds in sedimentary rocks. Mirabilite ( $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ ) and thenardite ( $\text{Na}_2\text{SO}_4$ ) are the common sodium sulfate minerals. Mirabilite forms needle-like crystals resembling the pyroxenes in shape. It generally occurs as crusts or efflorescences. It is a very soft, white mineral with a vitreous luster, and it ranges from transparent to opaque. It is quite soluble in warm water, but much less so in cold water. When exposed to dry air it loses its water of crystallization and falls to a fine powder.

Thenardite is a white or brownish mineral that forms euhedral crystals and masses of anhedral grains. It is very soluble in water, and its solubility decreases as the temperature is raised. Either mirabilite or thenardite can be prepared by evaporating a solution of sodium sulfate. Below a temperature of  $32.38^\circ\text{C}$ . crystals of mirabilite form, while at higher temperatures thenardite crystallizes.

Other minerals that contain sodium sulfate are glaserite ( $3\text{K}_2\text{SO}_4 \cdot \text{Na}_2\text{SO}_4$ ), blödite ( $\text{MgSO}_4 \cdot \text{Na}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$ ), glauberite ( $\text{Na}_2\text{SO}_4 \cdot \text{CaSO}_4$ ), hanksite ( $9\text{Na}_2\text{SO}_4 \cdot 2\text{Na}_2\text{CO}_3\text{KCl}$ ), and burkeite ( $2\text{Na}_2\text{SO}_4 \cdot \text{Na}_2\text{CO}_3$ ).

**Localities.** In California, sodium sulfate is currently produced only from the brines of Searles Lake which are treated at the plants of the American Potash & Chemical Corporation and the West End Chemical Company. These operations are described in the section on salines in this bulletin. The American Potash & Chemical Corporation produces two grades of sodium sulfate: salt cake, containing 97 percent  $\text{Na}_2\text{SO}_4$ ; and desiccated sodium sulfate, containing 99.3 percent  $\text{Na}_2\text{SO}_4$ . The West End Chemical Company produces a single grade containing about 99½ percent  $\text{Na}_2\text{SO}_4$ .

The American Potash & Chemical Corporation also recovers sodium sulfate in a separate operation by spraying raw brine in a prepared area on the lake surface. The brine is thus chilled sufficiently for the crystallization of mirabilite, which falls from the spray as a solid. Spraying is done only in winter because during the summer the brine is not chilled enough in the hot air to cause the crystallization of mirabilite. The crude mirabilite is scraped up, brought to the main plant, and refined in the soda products process to the grades noted above. Outside of California, natural sodium sulfate is produced in Texas, Wyoming, and western Canada. It is or has been produced in Chile, Italy, Spain, Russia, Egypt, and parts of Asia.

Deposits at several other localities in California have yielded sodium sulfate in the past. From 1937 until late in 1948, it was produced by Dale Chemical Industries, Inc., and its predecessors at Dale Lake, San Bernardino County (Wright et al., 1953, pp. 220 and 240, 241). This deposit was first explored by drilling between 1920 and 1924. Dale Lake contains lenticular beds of mixed thenardite and halite separated by impervious clay. Thenardite-halite lenses are as much as 40 feet thick, and the salt-clay series extends to at least 308 feet, the deepest hole drilled. The salt beds are permeated with sodium chloride-sulfate brine containing about 22 percent NaCl and 7 percent  $\text{Na}_2\text{SO}_4$ . In the early 1940's some thenardite was mined from an outcrop on the southwest side of the lake. A marketable product proved to be difficult to produce from the bedded material, and the principal production has been from brine obtained from wells sunk to a depth of 250 feet in the thenardite-halite beds. Several schemes have been employed for recovering sodium sulfate from the brine. In the most recent process mirabilite, obtained by spraying the brine in winter, was converted to anhydrous sodium sulfate by heating with steam and the addition of sodium chloride. The sulfate-free brine from this process was evaporated in solar ponds for the recovery of common salt. Although Dale Lake probably contains several million tons of sodium sulfate, its recovery is hampered by the comparatively long distance from Amboy, the nearest railroad loading point.

In the Durmid Hills, Imperial County, thenardite and blödite occur in folded Tertiary shale and sandstone beds (Sampson and Tucker, 1942). The sulfates are exposed over an area half a mile wide and about 3,000 feet long, and beds 3 inches to 5 feet thick have been encountered. Some mining by open cut has been done, but the operation was abandoned because of the high magnesium sulfate content (4 percent).

Sodium sulfate has been obtained from Soda Lake, San Luis Obispo County, which occupies the lowest part of an undrained basin between the Caliente and Temblor Ranges (Franke, 1935; Gale, 1914). A crust of mirabilite, little more than an inch thick, covers an area of from 2,800 to 3,000 acres, but in filled channels the mirabilite is up to 6 feet thick. Beneath the crust is a brine-permeated, greenish-gray mud containing crystals of mirabilite and blödite. The deposit, although thin, is estimated to contain over a million tons of mirabilite. Some production was obtained by dissolving the crust in place, collecting the brine, and recrystallizing sodium sulfate in ponds by solar evaporation.

Mirabilite crystals are disseminated through the mud in parts of Danby Lake, San Bernardino County (Wright, 1953, tabulated list, p. 190). A few carloads of sodium sulfate crystals have been mined and shipped from small mushroom-shaped deposits in the central part of Danby Lake west Saltmarsh Station.

Additional deposits have been noted in Black Basin in Old Dad Mountains and at Emerson Lake, 60 miles east at Victorville, California, but neither deposit has been developed (Tucker and Sampson, 1930, p. 322).





FIGURE 1. Open cut at Bertram sodium sulfate deposit, Imperial County. Thenardite and blödite occur in folded Tertiary shale and sandstone beds. The deposit was last worked about 1940.

Sodium sulfate is present in the brines of Owens Lake and Mono Lake but is not recovered commercially.

**Methods of Recovery.** Most natural sodium sulfate is recovered by techniques that are more related to the chemical industry than to the mining industry. In California at least two deposits of the natural mineral thenardite, the surface deposit at Dale Lake and the Durmid Hills deposit, have been worked by open cut methods. Neither was pure enough for the recovery of a marketable product by techniques such as crushing and screening.

Sodium sulfate is commonly recovered from natural brine or, more rarely, from solutions prepared by dissolving impure or disseminated sodium sulfate minerals in water. Under favorable conditions mirabilite or glauber salt ( $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ ) can be recovered from brine by solar evaporation. More often advantage is taken of the temperature-solubility relations of sodium sulfate to recover mirabilite by chilling the brine, which in many cases can be accomplished by refrigeration or by spraying.

Anhydrous sodium sulfate is produced by driving off the water of crystallization from mirabilite, a comparatively difficult step. Above about 90 degrees F. the solubility of sodium sulfate decreases with increasing temperature, and most types of dehydrators are inefficient because of the build-up of scale on heat transfer surfaces and walls. In one successful method, anhydrous sodium sulfate is crystallized from a solution of mirabilite in water by burning fuel below the surface. In another, the addition of sodium chloride to a hot sodium sulfate solution causes the crystallization of anhydrous sodium sulfate.

**Uses.** The principal uses of sodium sulfate are in the manufacture of sulfate or kraft pulp for paper, synthetic detergents, and glass, and in stock feeds. In California the production of sodium sulfate is substantially greater than the consumption, and most of the produc-

tion is shipped out of the state to kraft pulp mills. The pulp industry consumes 70 to 80 percent of the United States' supply of sodium sulfate. In the kraft or sulfate process for making pulp, sodium sulfate is reduced with carbonaceous material; and a solution containing sodium sulfide, caustic soda, and sodium carbonate is obtained. Wood chips are cooked in this solution to dissolve the lignin and free the cellulose fibers. This process can employ a relatively low grade of sodium sulfate; a purity of 95 to 97 percent  $\text{Na}_2\text{SO}_4$  is satisfactory.

The greatest uses for sodium sulfate in California are in synthetic detergents and common lime-soda glass. Additional amounts are used in ceramics, metallurgy, and for stock feeds. In detergents sodium sulfate serves as a builder and bulking agent; desiccated sodium sulfate of 99 percent or higher grade is specified. In American glass making plants, sodium sulfate is a minor ingredient in the batch used for refining the bath. Commonly sodium sulfate of 98 percent purity is specified.

**Price.** In 1955 the price of salt cake in bags was \$26.50 per ton f.o.b. Trona.

**Marketing.** Most sodium sulfate enters the market as salt cake or crude anhydrous sodium sulfate containing 92 to 99 percent  $\text{Na}_2\text{SO}_4$ . The name salt cake is also applied to deposits of the natural mineral thenardite. Other commercial sodium sulfate compounds include desiccated or anhydrous sodium sulfate, which has a  $\text{Na}_2\text{SO}_4$  content of 99 percent or more, and glauber salt ( $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ ). Glauber salt is used for special purposes in comparatively small amounts. Even though it is an intermediate product in the West End Chemical Company's process, none is sold. Sodium sulfate products are sold in earload lots directly to the consumers by producers' salesmen. Less than earload lots are handled through chemical supply houses.

Much of the supply of sodium sulfate is a by-product of several chemical processes. Of a total United States output in 1953 of about one million tons, 34 percent came from the Mannheim process of manufacturing hydrochloric acid from sulfuric acid and salt, 25.1 percent from natural deposits, 25.0 percent from the manufacture of viscose rayon, 10 percent from the manufacture of chromium chemicals, and 5.9 percent from miscellaneous chemical processes including the manufacture of formic acid, boron chemicals, lithium chemicals, and phenol sulfonation (Chem. Eng. News, 1955). The supply of sodium sulfate tends to vary with the activity of these industries which in turn depends upon complex and seemingly unrelated economic factors. Hydrochloric acid, for example, is currently produced by the direct synthesis of chlorine and hydrogen as well as by Mannheim plants. Chlorine is commonly obtained by the electrolysis of brine, a process which also yields caustic soda. The supply of sodium sulfate from Mannheim plants depends, therefore, not only on the demand for hydrochloric acid but also on factors such as the availability of sulfuric acid and the relative demand for chlorine and caustic soda.

About the year 1927, plants making hydrochloric acid by the direct synthesis of chlorine and hydrogen partly displaced the Mannheim acid plants, and the supply of by-product sodium sulfate declined. At the same time there was an increasing demand for sodium sulfate in the



kraft pulp industry. Imports, particularly from Germany, satisfied the demand for a time, but since the outbreak of World War II imports have been small. Interest in natural sodium sulfate has been stimulated. Since the war, the output of by-product sodium sulfate, which is imperfectly correlated with demand, has fluctuated.

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## SPECIALTY SANDS

By THOMAS E. GAY, JR.

California's 1955 output of 64,815,628 short tons of sand and gravel, valued at \$66,351,853, led the nation. In recent years sand and gravel has continuously ranked third in value among the state's mineral products, and was headed only by petroleum products and cement. About 99 percent of this output is used as aggregate, but in 1952, the most recent year for which figures are available, California yielded at least 587,562 tons of specialty sands, valued at \$1,938,415 (Otis and Jensen, 1955, pp. 4-8). About 54 percent of the specialty sand tonnage was used in glass making, about 21 percent for sandblasting, about 12 percent for engine sand, about 10 percent for foundry sand, about 3 percent for filter sands and other specialty sands.

The special sands used in California are obtained mostly at localities within the state and consist largely of material from Recent beach and dune deposits and early Tertiary sandstone.

California contains no known sand deposits that compare in quality with the higher grade sand in the eastern states, such as the Ordovician St. Peter sandstone which is extensively exposed and quarried near Ottawa, Illinois, and which consists almost entirely of nearly perfectly rounded quartz grains. It is widely used in the United States for exacting specialty sand purposes. Despite high transportation costs, at least 25,000 tons of this sand are brought into California each year, mainly for steel foundry and glass-making purposes. Several tens of thousands of tons of specialty sand also are brought into the state each year from Nevada.

Industries that use specialty sands are concentrated in heavily populated areas, such as the San Francisco and Los Angeles areas where nearly all glass, foundry, and sandblasting sand is used. Engine and filter sand, and some of the minor types of specialty sands, are used over wider areas of the state.

*Nature of Specialty Sands.* The term "specialty sand" (or "special sand") is applied to sand used for purposes other than for aggregate, ballast, or fill. Specialty sands generally have rigid physical and chemical specifications, and are used in much smaller quantities than ordinary sand. Some specialty sands include particles of gravel size (larger than a quarter of an inch).

Most specialty sands are obtained from the purest available sand deposits that can be economically worked. A high content of quartz makes the sand physically durable and chemically inert, and also provides silica as an ingredient of glass and soluble silicates. Clay is generally undesirable mainly because it coats sand grains and interferes with the usefulness of the sand. Only in naturally bonded foundry sands is clay a desired admixture. Both clay and iron-bearing minerals constitute chemical impurities in sands for use in the manufacture of glass and soluble silicates.

Sand from most specialty sand deposits can be used in several ways. A single deposit, for example, could yield sand suitable for sandblasting sand, engine sand, or foundry sand. Sands from some deposits are especially suited to a single use, and hence command rela-

tively high prices. The purest quartz sands are most prized for use in glass. Some clay-rich sands are used only as naturally bonded foundry sands, and "ganister."

Uses such as glass and soluble silicate manufacture require sand so clean that rigorous cleaning and beneficiation are ordinarily required. Sand to be used for less exacting purposes, such as for sandblasting and engine sand, commonly require little or no washing. Sand from some deposits is clean enough and of the right size for these uses without any processing.

Although nearly all clay-free special sand is suited for use as aggregate sand (concrete and plaster sand), the sands of higher quality are more valued as specialty sands. Plaster sand, also discussed in this volume as a type of aggregate, is mentioned under specialty sands because its specifications are similar to those of specialty sands, and it is obtained from many of the specialty sand deposits in California.

For most uses, the physical properties of specialty sands are more important than chemical properties. The chemical composition is held to rigid specifications only in the production of glass and soluble silicates. For such uses as sandblasting, hardness and durability are the essential characteristics; in others, such as filter media, close size grading is essential. High temperature of fusion is desired in sands for foundry and certain ceramic uses, and the presence of a certain proportion of clay is essential in naturally bonded sand for foundry use.

*Deposits and Operations in California* (Table 1). In California, as well as elsewhere, deposits from which specialty sands can be mined are much less common than the deposits that contain aggregate-grade material. In California, most specialty sand is obtained from Recent beach and dune deposits, and from Tertiary sedimentary rocks; relatively minor quantities of Recent alluvial sand are processed for specialty uses.

Recent beach and dune sands along the Pacific Ocean have constituted the principal source of specialty sands in California. In general these sands contain a lower proportion of quartz, and a higher proportion of feldspar, dark mineral grains, and rock fragments than the Tertiary sandstones that are mined for high-silica specialty sands. Beach sands, therefore, are used mostly for sandblasting, engine, and foundry sand, and for minor applications that do not require high-purity silica sand. Most beach sand deposits are measurable in many millions of tons, have little or no overburden, and can be mined inexpensively.

Most of the beach and dune sand that is mined in California for specialty uses is obtained from two areas in Monterey County; one is immediately southwest of Pacific Grove, and the other is along the shore of Monterey Bay, north of Monterey. The deposits southwest of Pacific Grove are unlike other beach sand deposits in California because of their uncommonly white color, and general lack of clay, iron-bearing minerals, and rock fragments. They consist of about 53 percent quartz grains; 46.5 percent feldspar, and 0.5 percent other



Table 1. *Specialty sand deposits in California.*

*Deposit	Location	Description of deposits	Principal uses	Operating data	Remarks and references
<b>A. Recent Beach and Dune Sands</b>					
1. Del Monte properties. 2. Owens-Illinois.	Pacific Grove, Monterey County.	Unconsolidated Recent dune sands that extend about 6 miles along the coast and about one mile inland. Most of sand is unusually white and clay-free; reportedly contains about 53 percent quartz, 46.5 percent feldspar, 0.5 percent other minerals.	Glass; clay-free foundry sand; silica flour for foundry, and ceramic uses.	Scraper, clamshells and conveyor belts bring sand to plants, where it is screened, scrubbed, tumbled, washed, dried, and treated in magnetic separators. One producer installed flotation system in 1952 to remove iron minerals and to separate quartz and feldspar.	Continuous production of specialty sand since prior 1920. Principal source of clay-free foundry sand in California. (Wright 1948, pp. 44-45; Mineral Information Service, June 1954, pp. 2, 4-8; Aubury 1906, p. 278; Latzore 1923, pp. 54-55; Lenhart 1952; Messer 1954; Sampson and Tucker 1931, p. 440; Huguenin and Castello 1921, p. 157.)
3. Lapis. 4. Pratto. (Several localities and producers).	Monterey Bay, Monterey County.	Unconsolidated Recent dune and beach sands that extend along the east shore of Monterey Bay, mainly worked in the ten-mile section from Del Monte to Lapis. Sand is highly feldspathic and iron-stained, rather coarse-grained.	Sandblasting; clay-free foundry sand; concrete and plaster sand.	Dragline scrapers move beach sand, commonly from below sea-level, to plants near shore where it is screened and washed. For some uses sand is dried.	Exceptionally high permeability, some grades as high as 475. Since 1946 its use as foundry sand has declined. Transported in bulk by ship to various Pacific Coast shipyards for sandblasting. (Wright 1948, pp. 45-46.)
5. Oceano Beach.	Oceano Beach, San Luis Obispo County.	Unconsolidated sand dunes that extend for several miles along the shore south of Pismo Beach and as much as one mile inland. Highly feldspathic sand, rather fine-grained.	Clay-free foundry sand; locally for sandblasting and engine sand.	Power shovel or dragline places sand in bins; screens remove organic debris. Drying facilities being installed in 1955.	Unusually flexible sand, suited to various foundry uses. Very low base permeability (85). (Wright 1948, pp. 47-48.)
6. El Segundo. (Several localities and producers.)	El Segundo area, Los Angeles County.	Unconsolidated, highly feldspathic dune sands that extend about 10 miles along Santa Monica Bay between Playa del Rey and Palos Verdes Hills, and about two miles inland.	Sandblasting; engine sand; clay-free foundry sand.	Front-end loaders fill trucks for delivery to storage yards. Engine sand loaded on gondola cars. Most sand sun-dried and unscreened, except for removal of organic debris.	Characteristics similar to Monterey Bay sand. (Gay and Hoffman, 1954, p. 563; Wright 1948, p. 43.)
7. San Francisco.	San Francisco Beach, San Francisco County.	Unconsolidated dune sand, with high proportion of dark minerals and organic impurities, exposed (before housing encroachments) for many square miles in the beach areas of western San Francisco.	Clay-free foundry core sand; various local uses.	Mechanical loader filled bins to load trucks for haul to job. No processing except removal of vegetable matter.	Principally used for relatively unexact foundry purposes, for cores. Expansion of housing development terminated production in 1950. (Lawson 1914; Wright 1948, pp. 46-47.)
<b>B. Recent Alluvium</b>					
8. Sacramento Red Molding Sand (Cañon Co.). (Inactive since 1951.)	North Sacramento, Sacramento County.	Unconsolidated uppermost layer of Quaternary floodplain alluvium; contains sufficient common clay to be used in brick-making.	Naturally bonded foundry sand.	Removed by bulldozer and trucked directly to foundries without processing.	Mainly used in Southern Pacific Railroad Company foundry to make gray iron car wheels and engine parts. Deposit depleted, inactive since 1951. (Carlson 1955, pp. 170-171; Wright 1948, p. 58.)



9. Mission Red; San Francisco 440 Molding Sand. (Several localities and producers.)	Mission district, San Francisco Co.; South San Francisco, San Mateo County.	Unconsolidated reddish-brown crudely stratified alluvial capping as much as 20 feet thick, that overlies weathered Franciscan rocks in large areas in San Francisco and South San Francisco.	Naturally bonded foundry sand.	Removed by various open pit machinery; in part sun-dried, and screened before use; in part trucked directly to foundries.	Used principally for heavy iron and brass castings; commonly blended with clay-free sands. Inactive since early 1950's because reserves covered by new construction. (Lawson 1914; Wright 1948, pp. 50-60, 61-62.)
10. Los Angeles Molding Sand.	Elysian Park, Los Angeles, Los Angeles County.	Unconsolidated Recent alluvial ravine fill, as much as 50 feet thick, overlying Pliocene marine sandstone.	Naturally bonded foundry sand.	Excavated and loaded on trucks by Spier-wells loader; trucked to foundries without processing.	Byproduct of excavation for building sites. Reserves uncertain because of building encroachments. (Gay and Hoffman, 1954, p. 563; Wright 1948, pp. 50-51.)
11. Torrance-Redondo Molding Sands. (Several localities and producers.)	Torrance-Redondo area, Los Angeles coastal plain, Los Angeles County.	Unconsolidated, massive and stratified flat-lying beds of Quaternary valley-floor alluvium; clay content ranges widely.	Naturally bonded foundry sand.	Excavated by power shovels and trucked directly to foundries or to plants for milling, blending and storage prior to use.	Broad variety of sand types in this area enables their usage in various iron casting applications, from heavy castings to soil pipe. (Gay and Hoffman 1954, p. 563; Wright 1948, pp. 51-54.)
<b>C. Early Tertiary Sandstone</b>					
12. Owens-Illinois (Gladding, McBean.)	Ione, Amador County.	Poorly consolidated, gently-dipping, nearly massive 70-foot thick bed of Eocene Ione formation, yields about 60 percent quartz sand, 35 percent clay, 5 percent heavy minerals.	Flint glass sand; (high grade clay is co-product).	Quarried by dragline, transported as slurry to plants where liquid cyclone, screening, flotation, and drying processes are employed.	Joint silica sand-clay production commenced 1955. Finished silica sand contains 0.04 percent iron or less. (Allen 1929; Mineral Information Service, August 1956, pp. 1-5.)
13. Pacific Clay Products.	Camanche, Calaveras County.	Poorly consolidated, gently-dipping, crudely stratified section of uppermost Eocene Ione formation, consists of about 70 percent quartz sand, 20 percent feldspar sand, 5 percent clay, and 5 percent heavy minerals. Workable to 130-foot depth.	Flint glass sand; feldspar and clay are co-products.	Mined by hydraulic means; flows as slurry to plant where screening, liquid cyclone, attrition scrubbing, screening, classifying, flotation, filtration, drying and magnetic separation processes are employed.	Plant built in 1955-1956. Finished sand contains 0.05 percent iron or less. Deposit and operation similar to Owens-Illinois operations above. (Allen 1949; Mineral Information Service, August 1956.)
14. Tesla. (Livermore Ganister.)	Tesla-Corral Hollow area, Alameda County.	Poorly consolidated bed of fine-grained, thinly cross-bedded, white sandstone of Middle Eocene marine Tesla formation contains 75 to 95 percent quartz sand, 10 to 30 percent feldspar. Usable sand bed is 15 to 20 feet thick, and dips 60° between coal seam and clay bed.	Glass sand for containers (prior 1910); naturally bonded foundry sand ("Livermore ganister").	Glass sand mined underground, via 500-foot adit, washed and tumbled to remove clay. Livermore ganister also mined by underground methods, but processed only by hammer milling before use.	High-grade fire clay and coal formerly mined from this formation at same locality. Ganister used minily for ladle and cupola furnace patching (Huey, 1947; Allen 1949; Wright 1948, pp. 48-50.)
15. Brentwood area. (Several localities and producers.)	Brentwood area, Contra Costa County.	Compact, poorly consolidated fine-grained quartz-rich Middle Eocene marine sandstone in belt traceable for 20 miles northeast of Mt. Diablo. Usable layer, 60 feet thick, dips 30° between sandstone walls at one deposit.	Clay-free foundry sand; glass sand for containers, and soluble silicates.	Underground (room and pillar) and open-pit mining methods used; raw sand trucked to plant where screening, washing, classifying, and chemical leaching methods were used to remove clay and reduce iron content to 0.045 percent or less.	Depletion of easily accessible near-surface reserves contributed to cessation of operation in 1942. (Davis and Vernon, 1951, pp. 580-584; Sampson and Tucker 1931, pp. 436-437.)



Table 1. *Specialty sand deposits in California.—Continued.*

Deposit	Location	Description of deposits	Principal uses	Operating data	Remarks and references
<b>C. Early Tertiary Sandstone</b> —Continued					
16. Nortonville-Somersville area, (Several localities and producers.)	Near Antioch and Pittsburg, Contra Costa County.	Poorly consolidated, massive, middle Eocene marine sandstone (similar to material mined in Brentwood area, above). Usable material, to beds 25 to 50 feet thick, dips about 25°.	Steel foundry sand; glass sand (prior to 1945).	Open-pit and underground methods used; both require blasting. For glass manufacture, the sand was crushed, washed, dried and screened. For foundry use, the sand is disintegrated, scrubbed, washed and classified.	Coal formerly obtained from extensive operations nearby, and from sand-yielding workings. California's principal source of high-silica foundry sand for steel casting. (Davis and Vernon, 1931, pp. 582, 583; Wright 1948, pp. 40-42.)
17. Owens-Illinois.	Corona, Orange County.	Poorly consolidated, coarse-grained, nearly flat-lying, thin-bedded white sandstone that forms basal unit of Paleocene Silverado formation, contains about 60 percent quartz sand, 40 percent clay, silt and scattered pebbles. Deposit worked to 120-foot depth.	Glass sand; formerly foundry and sand-blasting.	Open-pit excavation methods, using carryall scrapers; conveyor belts transport sand to plant where attrition scrubbing, screening, washing, and magnetic methods are employed to remove clay, pebbles, and iron-bearing minerals.	Principal source of glass sand in southern California. (Gray 1953, p. 93; Stauffer 1945; Tucker and Sampson 1945, pp. 163-164.)
18. Crystal Silica Co.	Oceanside, San Diego County.	Poorly consolidated, white, gently-dipping strata of Eocene marine Tejon formation include layers of usable sandstone as thick as 40 feet, separated by lenses of silt and clay. Usable material consists of about 65 percent quartz grains, 15 percent feldspar, 20 percent clay and silt, with minor content of heavy minerals.	Plaster sand; sand-blasting, engine, other uses; glass sand since 1954.	Open-pit operations; stripping and mining with bulldozers and carryall scrapers; material conveyed to plant as slurry, for treatment in trommel screens, liquid cyclones, and drying kilns to remove iron-bearing and fine materials.	Plant expanded and remodeled in 1954 to produce sand pure enough for use in glass. (Pacific Coast Ceramic News, December 1953, p. 17; Sampson and Tucker 1931, pp. 446-448; Tucker and Reed 1939, p. 51; Woodford 1925.)
19. Trabuco Canyon. (Several localities and operators.)	Trabuco Canyon and El Toro areas, Orange County.	Poorly consolidated, crudely stratified, gently-dipping, clay-rich sandstone of Paleocene Silverado formation yields china clay and quartz sand. Usable material is at least 40 feet thick.	Naturally bonded foundry sand ("Trabuco ganister"); clay-free foundry sand; silica flour.	Open-pit excavations; after blasting, material loaded on trucks by power shovels for haul to plants where disintegration, washing, and settling methods separate clay and quartz sand. Magnetic separators remove iron minerals. Quartz sand ground to silica flour in pebble mills. Ganister sold unprocessed except for crushing.	Output of area has increased notably since 1950. Co-product is high-grade china clay. Ganister is used mainly for ladle lining and cupola furnace patching. (Wright 1948, pp. 54-55.)
<b>D. Late Tertiary and Pleistocene Sandstone</b>					
20. Millbrae Blended Molding Sand.	Hills west of Millbrae, San Mateo County.	Unconsolidated, yellowish, poorly stratified material as much as 20 feet thick, apparently the oxidized portion of an underlying gray marine sandstone of the Pliocene Merced formation.	Naturally bonded foundry sand.	Removed by power shovel, trucked to plant where it is hammer-milled to pass 1/8-inch sieve, and blended with other materials for foundry use.	Obtained from excavations for fill for large construction projects; completion of freeway terminated operability in early 1950's. (Lawson 1914; Wright 1948, pp. 60-61.)



21. Santa Barbara Molding Sand.	Goleta, Santa Barbara County.	Poorly consolidated bed of uniformly yellow-colored and even-grained sandstone in Pliocene marine sedimentary section. Usable clay-rich layer, 20 to 25 feet thick, dips 40° between liney sandstones.	Naturally bonded foundry sand.	Selective open-pit mining by power shovel; trucked to mill for mulling before use.	Inactive since deposit exhausted to property lines about 1950; nearby buildings limit pit. (Wright, 1948, p. 63.)
22. Lompoc Molding Sand.	Between Lompoc and Buellton, Santa Barbara County.	Horizontal, Pleistocene marine sandstone, covered by ten feet or more of clay-deficient sandstone. Usable material, 5-feet thick, is of uniform grain size and mineral content, but contains local light buff concretin-ary layers.	Naturally bonded foundry sand.	Open-pit operations; sold without processing.	One of most refractory natural sands produced in California. Increasing depth of overburden led to cessation of operations about 1950. (Wright 1948, pp. 63-64.)
23. Ventura Molding Sand.	Ventura, Ventura County.	Unconsolidated, clay-rich Pleistocene marine sandstone. Usable bed, 100 feet thick, dips 47° between clay-poor sandstones. Usable material is light tan, slightly calcareous, and constant in grain size and mineral composition.	Naturally bonded foundry sand.	Power shovel moves material into rotary screens which separate it into several size ranges; distributed by truck.	Similar to San Diego molding sand (below); extremely fine-grained; 63 percent passes 270-mesh sieve. (Wright 1948, pp. 64-65.)
24. Santa Ana Molding Sand.	Irvine Ranch area, near Tustin, Orange County.	Light yellow, unusually fine-grained sand (Donco Light); reddish sand, with wide range of grain sizes, and 20 percent clay content (Donco Heavy); and intermediate types of sand occur in Miocene, Pliocene, and/or Quaternary beds widely exposed in the area.	Naturally bonded foundry sand.	Quarried by power shovel, trucked to plant where pebbles are removed by screens, and large lumps are crushed by rolls.	Wide range of properties and uses of the several sands produced in this area. (Wright 1948, pp. 55-57.)
25. Riverside Molding Sand. (Several localities and producers.)	Along Santa Ana River, west of Riverside, Riverside County.	Poorly consolidated, unstratified layer of reddish clay-rich sand, covers Quaternary terrace. Usable material, 6 to 8 feet thick, underlain in part by silty sediments and in part by granitic rock; overburden is one-foot thickness of clay-poor sand.	Naturally bonded foundry sand.	Bulldozer removes and loads sand on trucks for haul to plant where it is milled or pulverized by rolls, then stored for use.	(Wright 1948, pp. 57-58.)
26. San Diego Molding Sand.	San Diego, San Diego County.	Crudely stratified horizontal layer, at least 60 feet thick, of yellowish buff clay-rich Pliocene sandstone which underlies large part of San Diego. Overburden is about 4 feet thick. Portions of section contain abundant shell fragments.	Naturally bonded foundry sand.	Open-pit operation; power shovel cuts face down, then hand shovel is used to remove concretions, which are screened separately. Trucks carry sand to shipping point.	One of California's finest-sized natural sands; 65 percent passes 270-mesh sieve. (Wright 1948, pp. 58-59.)

\* See Figure 1 for locations.



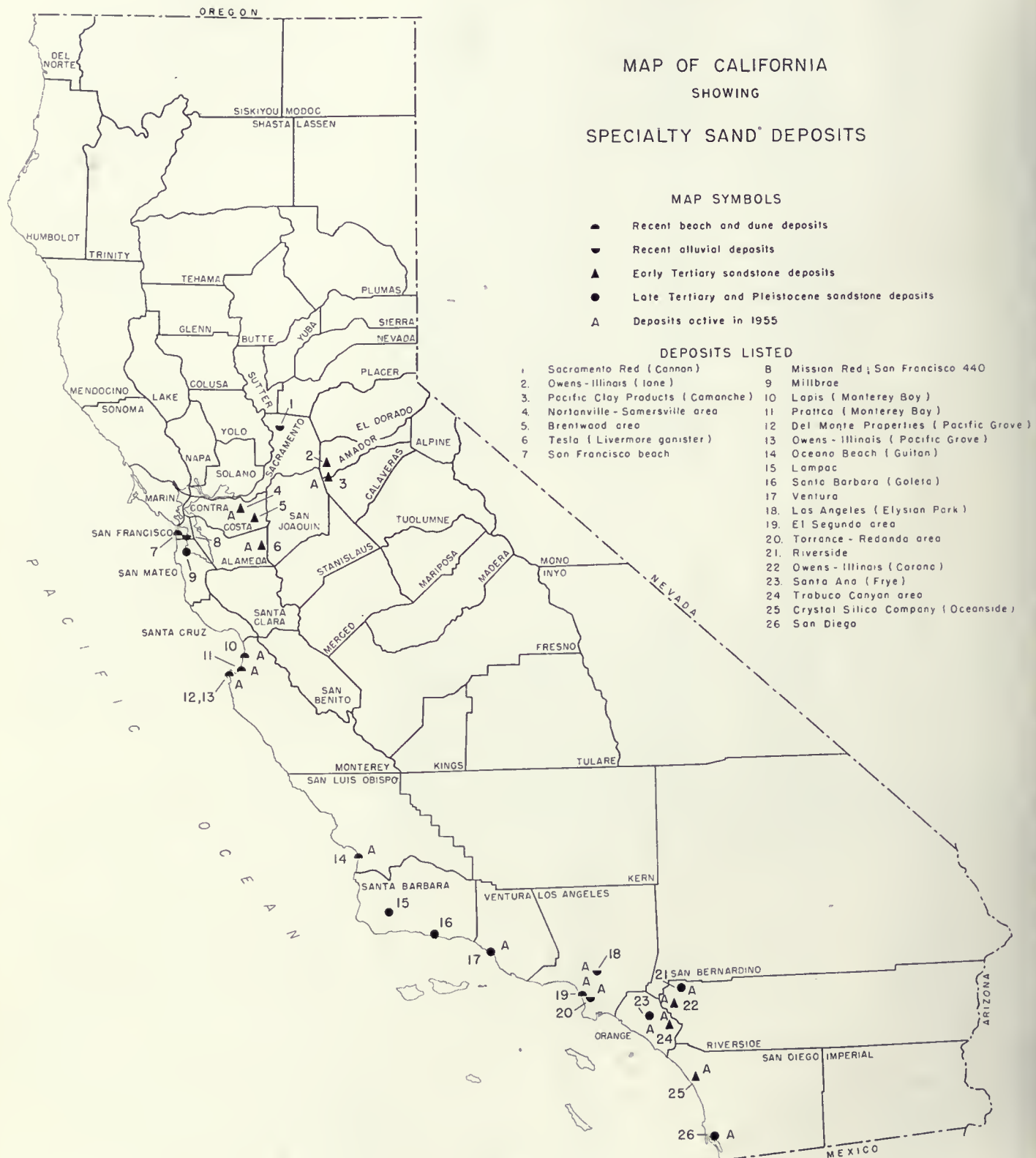


FIGURE 1.



minerals, including biotite, ilmenite, garnet, zircon, and monazite (Valentine, P. C., personal communication, 1954). Nearly all sand grains pass a 20-mesh sieve, and one or two percent pass a 100-mesh sieve. Some of this sand, after washing and drying, is used as clay-free foundry sand. Some of it is beneficiated to remove iron-bearing minerals; part of the iron-free product is separated into nearly pure fractions of quartz and feldspar. The iron-free sand is used mainly for glass manufacture and stucco. The quartz product is used for glass and foundry purposes, and, when finely ground, for ceramic, refractory, and abrasive uses, and as a filler. The feldspar fraction is used mainly in the glass, ceramic, and cleanser industries.

The east shore of Monterey Bay is formed entirely of dune sands, which consist largely of feldspar grains, and have appreciably higher iron content than the Pacific Grove sand, both as ferromagnesian minerals and as ferruginous coatings on the quartz and feldspar grains. This sand is sold with no treatment except washing and screening, mainly for use as sandblasting and foundry sand, and for plaster and concrete sand.

At Oceano Beach, San Luis Obispo County, a dune area several square miles in extent yields clean feldspathic sand that is unusually fine-grained, and closely graded in grain size; about 90 percent of the grains are retained on the 100- and 140-mesh sieves. This sand is sold unprocessed, mainly for use as foundry sand, but locally for sandblasting and engine sand.

At El Segundo, Los Angeles County, ordinary feldspathic dune sand is obtained for use as sandblasting, foundry, and engine sand. Much of the wet material is dried; otherwise little or no processing is done. The El Segundo sand is favored by its proximity to the Los Angeles market, and its resultant low transportation cost.

Most of the beach and dune sands in northern California contain large proportions of dark mineral grains and dark rock fragments, and have been much less ex-

tensively used as specialty sands than those from Monterey Bay, and southward.

In the 1950's all but a very small part of the specialty sand recovered from the beaches of California is being obtained in about 13 operations: two at Pacific Grove; four to six on Monterey Bay; one at Oceano Beach; and four to six at El Segundo.

In California, some of the highest quality silica sands are obtained from sedimentary sandstone formations of early Tertiary age. Although less pure than the silica sands mined in Illinois and Missouri, they form the principal source of supply for the glass industry of California. Tertiary deposits that have yielded sand for specialty uses include Paleocene deposits south of Corona, Riverside County, and in the Trabuco Canyon area, Orange County; and Eocene deposits near Ione, Amador County; Oceanside, San Diego County; Tesla, Alameda County; and in the Nortonville-Somersville and Brentwood areas, Contra Costa County.



FIGURE 3. Recent dune sand deposit about 7 miles south of Pacific Grove, Monterey County. Pit opened in 1955 by Del Monte Properties Company, as source of glass sand.



FIGURE 2. Recent dune sands at Pacific Grove, Monterey County, worked by Del Monte Properties Company and Owens-Illinois, mainly as source of glass sand. Deposit largely depleted by 1956. Belt conveyor and raw sand surge pile (left) of Del Monte Properties Company. (Photo courtesy Del Monte Properties Company).

These deposits consist essentially of quartz grains and clay, with a low percentage of partly decomposed feldspar, and very small proportions of heavy, resistant minerals such as garnet, epidote, zircon, magnetite, and ilmenite. They are exposed in belts that range from several thousand feet to several miles long, are ordinarily about 25 to 200 feet thick, and dip gently to moderately. They have been mined mostly by open-pit methods. If it is to be used for glass sand, the mined material requires beneficiation to remove clay and iron-bearing minerals. The high-quality clay recovered from the beneficiation of these sands in the Ione and Trabuco Canyon areas is valued for ceramic uses. Sand from these deposits is also used, with relatively minor treatment, for foundry sand and less common uses.

In 1956, ten operations were active in these high-silica sandstones of early Tertiary age. One was at Ione, Amador County; one at Camanche, Calaveras County; one near Corona, Riverside County; four in the Trabuco Canyon area, Orange County; one near Oceanside, San Diego County; one near Tesla, Alameda County; and one near Antioch, Contra Costa County. Those near Ione, Camanche, Corona, and Oceanside pro-



duced sand mainly for use in glass; those near Trabuco Canyon, Tesla, and Antioch, mostly produced foundry sand.

Post-Eocene Tertiary sandstones are very widespread and abundant in California, but they have not been extensively mined as sources of specialty sands. Their characteristically high feldspar content and the low quality of their contained clay prevent them from competing with early Eocene sandstones as sources of high quality silica sands or ganister.

Their relatively high degree of consolidation, and consequent high expense of preparation, makes them less desirable than dune sands as sources of sandblasting and engine sands. One of the higher quality later Tertiary sandstones is the upper Miocene Santa Margarita formation, which is quarried near Felton, Santa Cruz County, mainly for aggregate use. Pleistocene and Pliocene beds in Ventura County, and Pliocene beds in San Diego County, and west of Millbrae, San Mateo County, are sources of foundry sand.

*Mining Methods.* Almost all of the specialty sand produced in California is mined by open-pit methods (table 1). Blasting is required only in the relatively well consolidated Eocene sandstones obtained in the Trabuco Canyon, Tesla, Brentwood, and Nortonville-Somersville areas. Bulldozers and rippers are used to loosen material at Oceanside, Ione, and several of the naturally bonded foundry sand deposits in southern California. Excavating equipment includes power shovels, draglines, clamshell excavators, screw-type excavator-loaders, bulldozers, carryall scrapers, and slack-line cable draglines.

Hydraulic methods are used at Camanche, both to loosen the bedded sand, and to elevate loosened material out of the pit. Raw material is conveyed to the several plants as slurry pumped through pipes; on belt conveyors; in carryalls; or in trucks. Salable material is transported from treatment plants, or direct from deposits, by truck or rail.

Underground mining of special sands occurred only in the relatively thin, moderately to steeply dipping, quartz-rich Eocene sandstones in the Tesla, Brentwood, and Nortonville-Somersville areas, mostly prior to 1940. Adits as long as 2000 feet, and room-and-pillar systems of mining were reported (Davis and Vernon, 1951). The only underground specialty sand operation active in 1956 was the Livermore ganister deposit near Tesla.

#### UTILIZATION

In the period 1950 to 1953, about half of the 550,000 to 600,000 tons of specialty sands produced in California was used in the manufacture of glass, about one-fifth was used as a sandblasting material, one-eighth as foundry sand, and the remainder for filter sands, engine sand, and a variety of minor uses. Relatively minor tonnages are used as ceramic and refractory materials; nursery, aquarium, and sandbox sand; in golf sand traps, concrete pipe, and cigarette urns; and as filler, chinchilla dust, and roofing gravel.

*Glass Sand.* Glass, which consists essentially of silica ( $\text{SiO}_2$ ), requires pure silica sand as its principal ingredient. Unlike most specialty sands, glass sand is selected primarily for its chemical composition rather



FIGURE 4. Recent dune sand deposit at El Segundo, Los Angeles County, used mainly for sandblasting, engine, and foundry sand. Pit of Paramount Sand Company, 1954.

than its physical properties. Most of the many common types and grades of glass require sand with a maximum of silica and a minimum of iron. Feldspar, in amounts ranging up to almost 50 percent, is acceptable in some of the glass used for containers. "Amber" glass sand, which may contain from 0.05 to as much as 0.10 percent iron, is used in colored glass containers; "flint" glass sand, which contains a maximum of 0.04 percent iron, is required for all colorless glass, for containers or plate glass.

Excessive fines are undesirable because they carry impurities and also tend to be lost with the flue gases. Sands with rounded, angular, or subangular grains appear to be satisfactory (Wiegel 1947, p. 132).

A major concern of glass sand producers is the establishment and maintenance of consistent quality of the sand produced. Nearly complete mechanization of the glass manufacturing industry necessitates consistency of raw materials in order that glass-shaping machines may operate continuously and efficiently without frequent adjustment for variation in properties of the molten glass.

About 95 percent of California-made glassware consists of containers, either clear or colored; the rest is optical glass, general glassware (e.g. ash trays), and rolled, rib, and wire glass (e.g. shower doors). Despite the tremendous demand of California's large building industry, all window and plate glass is brought into the state. No plate glass manufacturing plants had been built here by 1956, mainly because known reserves of flint glass were considered insufficient to support this industry. Since 1952, however, methods and machinery have been developed for removing clay, and reducing the iron content of previously unsuitable sand. The consistent large-scale production of flint glass sand at Ione has shown that large portions of the extensive Ione formation are potential sources of sand from which plate glass could be made.

The output of the glass container industry in California has about doubled between 1945 and 1955, stimulated largely by the state's phenomenal population growth. Five new glass container plants were built in the state during this period, and existing plants were





FIGURE 5. Gently dipping clayey sandstone of Eocene Ione formation as exposed in test pit of Gladding, McBean and Company, and Owens-Illinois, near Ione, Amador County. (Photo by Mort D. Turner, 1949).

enlarged. Increased use of one-way containers, substitution of glass for metal containers, and general increase in consumption of bottle-packaged goods, especially soft drinks and beer, in the state have increased the demand for container glass.

Since World War II increasing amounts of high-grade silica sands obtained near Lake Mead, Nevada, have been brought into California for glass sand usage. An estimated one-third to one-half of the glass sand used in California in 1955 came from Nevada, despite railroad rates of about \$3.50 and \$5 per ton, to Los Angeles and San Francisco, respectively. The high-silica Nevada sand commonly is blended with feldspathic local sand to make container glass. The high transportation costs from out-of-state deposits have stimulated recent efforts to develop additional sources of glass sand in California.

**Abrasive Sand.** Included under abrasive sands are those used for sandblasting, sandpaper, stone-sawing, glass-grinding (banding), and sweeping compound. Nearly all of the output of abrasive sand in California is used for sandblasting (see section on abrasive materials in this volume).

Sandblasting involves the abrading or cleaning of surfaces by the impact of sand particles blown at high speed by jets of compressed air. In 1952, California yielded 121,070 short tons of abrasive ("grinding and polishing") sand, valued at \$372,611 (Otis and Jensen, 1955, p. 5). Nearly all of this was sandblasting sand produced from beach deposits in the Monterey Bay area, and from dunes near El Segundo.

Sandblasting sand commonly is held to rather broad specifications. It should be tough enough to resist crushing or shattering. Nearly pure quartz sands are generally

considered to be most practicable. An excessively fine-grained or soft admixture is undesirable. Small amounts of more expensive garnet sand and glassy mineral shot obtained as a byproduct of mineral wool manufacture, are used for some special metal finishing processes and the sandblasting of inscriptions and designs on polished



FIGURE 6. Gently dipping clayey sandstone of Eocene Ione formation, exposed in operating pit of Gladding, McBean and Company, and Owens-Illinois, near Ione, Amador County. Overburden stripped from left background. Dragline loads raw material in movable pit station (center) where it is mixed to slurry and pumped through pipes to fixed pump station (foreground) for pumping through pipes (left) to processing plants. (Photo courtesy Owens-Illinois, 1955).





FIGURE 7. Gently dipping sandstone of Palaeocene Silverado formation exposed in pit of Owens-Illinois near Corona, Riverside County. Carryall scrapers transport raw sand to base of inclined conveyor belts (left) which convey it across Highway 71 to plants (middle distance) where it is processed for use as glass sand. Inactive pit east of highway is at left of plant, behind raw sand surge pile.

stone monuments. Steel and cast iron shot are used in certain metal-finishing applications. Opinion is divided whether angular or rounded grains are more desirable; both are widely and successfully used. Four main sizes are in general use, although few California producers sell more than two. Disregarding small percentages of coarser and finer material, the nominal sizes are No. 1, 20 mesh to 48 mesh; No. 2, 10 mesh to 28 mesh; No. 3, 6 mesh to 14 mesh; and No. 4, 4 mesh to 8 mesh.

An estimated thousand tons of tough, uniformly sized sand approximately equivalent to No. 1 sandblasting sand, are consumed each year in California as an abrading agent for the sawing of marble dimension stone. Most

of the sand for this use is obtained from the El Segundo dune deposits, and is consumed in stone-cutting mills in the Los Angeles area.

An estimated 3,000 tons, or more, of clean, fine-grained, uniformly sized sand are used in California each year in sweeping compound, used in sweeping large buildings. The sand is used mainly to give weight and body to the compound; abrasive action is intended to be minor. Most of the state's sweeping compound is manufactured in the Los Angeles area, with sand from El Segundo dune deposits.

Although long ago sand grains were used as abrasive on sandpaper, sand has been almost completely replaced



FIGURE 8. View southward of Crystal Silica Company operation in Eocene Tejon sandstone near Oceanside, San Diego County. Pits seen behind and to right of plant (left center) were inactive in 1955. Portion of new pits seen at left, just past settling ponds in which used wash water is purified for reuse.





FIGURE 9. Moderately dipping middle Eocene sandstone exposed in pit of M. J. Marchio in Nortonville-Somersville area, south of Antioch, Contra Costa County. When washed, sand is used in steel foundry.

for this use by crushed garnet and artificial abrasives. No sandpaper is manufactured in California.

**Engine Sand.** Engine, or locomotive sand is used to (1) sand the track to provide traction under the drive wheels of locomotives and street cars, and, (2) sand soot from flues on oil-burner locomotives. Traction is by far the principal use. An estimated 75,000 tons or more of engine sand were produced in California in 1956.

As traction sand must be free-running, it is thoroughly washed to remove fines and foreign material. Both angular and rounded grains are equally effective under the drivewheels, but angular sand is preferred because rounded grains tend to roll off the rail before being crushed by the wheels.

Most of the engine sand produced in California is obtained from beach and dune deposits at El Segundo and Monterey Bay, although relatively minor tonnages are obtained from San Diego, Ventura, and Imperial Counties, and from alluvial deposits in the Great Valley.

**Foundry Sand.** In 1952, the output of foundry ("molding") sand in California totaled 61,209 tons, valued at \$208,140, an average value of about \$3.40 per ton (Otis and Jensen, 1955, p. 4). Foundry sands are those used to make forms for the casting of metal shapes by foundries. If used to make molds they are called molding sands; if used to make cores, to form hollow spaces in the casting, they are known as core sands. The main properties that determine the suitability of a sand for foundry use are (1) bond; (2) fineness and size distribution of sand grains; (3) refractoriness; and (4) durability.

All foundry sands require a binder, such as clay, to preserve the shape of the mold until the casting is poured. About two-fifths of the foundry sand that is

produced in California each year is bonded by clay that is a natural constituent in the sand. Such sand is said to be naturally bonded. About three-fifths of the foundry sand produced in California is clay-free. As carefully controlled proportions of binding materials are added to them, these sands are known as "synthetic." The binding materials include fire clay, bentonite, sea coal, pitch, resins, and cereals.

By varying the proportions of the constituents of synthetic sands, it is possible to control such properties as compressive, shear, and tensile strengths, deformation, flowability, and durability. As foundry practice has become increasingly exacting in recent years, the use of synthetic sands compared to naturally bonded sands, has increased greatly.

The grain-size and size distribution of foundry sands affect the permeability, as well as determine the ease with which the sand can be rammed when the mold is made. Permeability must be controlled to permit the escape of mold gases during casting, and to resist penetration by hot metal. Permeability varies directly with the size of the grains, the uniformity of grain size, and the degree of grain rounding.

The composition of the sand grains is the principal factor controlling the refractoriness of a sand, or its ability to withstand the casting temperatures without excessive fusion or vitrification. Pouring temperatures range from as low as 1,200° F. for aluminum castings, to more than 3,000° for steel castings. Naturally bonded sands, in which natural admixtures of alkali feldspars may lower the refractoriness, are generally used only for lower temperature castings. Sands consisting of at least 96 percent quartz, the most refractory of the minerals common in sand, are used for steel castings. For especially high-temperature castings special zircon sands are used; ilmenite and olivine sands have been suggested for this purpose (Ries 1948, p. 11).

Durability of a foundry sand is measured by the number of times it can be reused. Loss of strength occurs through dehydration and devitrification of its bonding clay. To return sand to its original condition a certain amount of binder must be added after each use. Naturally bonded sands tend to have lower durability than synthetic sands. Sand grains themselves must be durable enough to withstand the thermal shock of contact with molten metal as well as abrasion from milling, mulling and ramming.

Steel casting is most destructive of sand because of the high pouring temperature. Steel foundries that use all new sand consume about 2,000 to 3,000 pounds of sand per ton of casting. Foundries with facilities to reclaim used sand consume about 700 to 1,200 pounds of new sand per ton of casting. Gray iron foundries consume about one-half ton of new sand per ton of casting produced and non-ferrous casting requires much less. Because relatively low cost sands are used at such plants, the expense of installing reclaiming equipment is rarely justified.

Consumers require that a given foundry sand be of consistently uniform quality. Quality may be controlled by selective mining and screening at the pit; and by lump-crushing, drying, and blending by jobbers.

Core sands, unlike molding sands, are artificially hardened by baking prior to casting. To avoid distor-





FIGURE 10. Gently dipping Paleocene clay-rich sandstone exposed in pit of W. A. Schoeppe, south of Trabuco Canyon, Orange County. At least three other operators are also quarrying this material in nearby pits. Material is separated into high-grade clay and high quality silica sand for several uses; unprocessed it is "Trabuco ganister."

tion of the casting as it shrinks around the core during cooling, the core must have low hot strength and crumble readily after initial solidification. For this reason more than 0.5 percent clay is rarely permitted in cores, and cereal or oil binders which burn out during pouring are used.

Nearly all of the state's requirements of naturally bonded sands are produced here, but a large proportion of high-purity silica sands for steel foundries and for various synthetic sands are brought into the state, mainly from Illinois and Nevada. The gray iron industry, by far the largest of California's foundry industries, and malleable iron foundries use about half local and half out-of-state sand, mostly clay-free. About 70 percent of the sand used in the nonferrous foundries in California, including those that produce brass, bronze, aluminum, and magnesium castings, is from sources within the state and is principally of the naturally bonded type.

In 1955, the proportion of synthetic sands to naturally bonded sands used in California was about 2:1; approximately the reverse proportion pertained in 1945. Another trend, the use of finer sands, has come with improvements in binders and higher pressure molding

techniques that result in harder faced molds that require less binder and less water, and result in a decrease in mold gases and lower permeability requirements.

Ganister is highly refractory siliceous sedimentary rock, used for furnace linings, or a mixture of ground quartz and fire clay used for lining steel converters. In California the term ganister is applied to a natural mixture of high-silica sand and fire clay that is used as a refractory in ladle patching and furnace linings. "Trabuco ganister" is obtained at several localities in the Trabuco Canyon area, Orange County, and "Livermore ganister" is mined at a single property near Tesla, Alameda County.

*Filter Sand.* In 1952, a total of 18,277 short tons of filter sand, valued at \$53,762 or an average value of about \$3.00 per ton, were produced in California. Sand and gravel are widely used in filter beds especially in the treatment of municipal water supplies, purification of swimming pools, and in water-conditioning equipment. Related uses include sewage trickling media, for which gravel and crushed rock beds are used, and well-packing gravel, for which pebbles are used.



FIGURE 11. Plant of Owens-Illinois near Ione, Amador County, where Ione sand is processed for use as glass sand. (Photo courtesy of Owens-Illinois).





FIGURE 12. Plant of J. M. Marchio, near Antioch, Contra Costa County, where Eocene sandstone is processed for use in steel foundries. Material is disaggregated and washed in revolving drum (right foreground), loaded by sand drag (center) on belt conveyor for storage in bins.

In most communities of California, sand and gravel filter beds are used to remove sediment, suspended matter, and bacteria from municipal water supplies. The surface area, depth, and size grading of filter beds are functions of the capacity. All filter beds contain sand to perform the filtering action, and gravel to support the sand.

Filter gravel should have maximum permeability, so round particles are desired. It should consist of hard, durable, rounded particles of high specific gravity, with a minimum (e.g. less than 3 percent) of thin, flat, or elongated pieces. It should be washed and screened and contain not more than one percent of loam, clay, sand, shells, dirt, and organic impurities or other foreign matter.

Filter sand must be of fairly uniform size and within certain size limits. In practice both rounded and angular grains have been found to be satisfactory, but angular grains make a "tight" filter with reduced filtering capacity unless pressure is used to force water through it. Flat or elongated grains are undesirable, as are soluble grains. As the filter beds can be effectively cleaned many times without appreciable loss of sand, most plants, once constructed, require only minor additions of filter sand.

"Effective size," and "uniformity coefficient" are expressions used to describe the sizing of filter sand. Effective size is the size, in millimeters, of the screen opening just large enough to pass 10 percent of the sand by weight; 90 percent of the sand is larger than the effective size. The uniformity coefficient expresses the closeness of the size grading of the sample and is the ratio of the mesh size through which just 60 percent of the sample will pass, to the effective size. These values can be obtained from a cumulative screen analysis curve of a particular sand. Specified effective sizes of filter sand generally range from 0.35 to 0.54 millimeters; the uniformity coefficient is commonly specified in the range 1.55 to 1.60.

An estimated 25 to 30 thousand swimming pools, public and private, exist in California; 20,000 are in the southern part of the state. The specifications and sources of filter sand and gravel used in swimming pool filters are about the same as for municipal water filtration plants.

Filter beds also are used in some of the larger household and industrial water-softening systems, to retain finely divided water-softening chemicals. Many industrial concerns treat their used water in filter beds of various designs and capacity so that it may be used again. Several thousand tons of filter sand and gravel are obtained each year in California for each of these usages.

The trickling type of sewage treatment plant, in use mainly in smaller communities, utilizes porous beds of coarse gravel, crushed slag, or crushed stone as filter-like media to keep bacteria in contact with the sewage. Because new treatment plants are of other types, and because trickling beds last almost indefinitely without replenishment of the media, little or no demand exists in California for this material.

California's filter sand is produced almost entirely as a subordinate product at two localities: (1) near Ocean-side, in San Diego County; and (2) Monterey Bay, Monterey County. Minor amounts of washed concrete sand produced by commercial aggregate plants in the Los Angeles area also have been used.

In California, filter gravel is produced near Carlsbad Beach, San Diego County, where rounded and polished beach pebbles are gathered and sacked by hand. Washed gravel, in appropriate sizes, produced by various commercial sand and gravel producers in the state, is also used.

Well-packing gravel, placed outside perforated casings of oil and water wells to prevent inflow of fine sediment from poorly consolidated strata, serves a filter-like purpose. Well-packing gravel should be well-rounded, hard, free of soluble particles, and closely graded to size. Commonly used sizes are, in Tyler sieve sizes, 16 to 30, 10 to 14, 8 to 10, 6 to 8, 5 to 7 mesh, and  $\frac{3}{16}$  inch.

Most of the several thousand tons of packing gravel produced each year in California comes from a Miocene marine deposit near WALTERIA, Los Angeles County, although smaller amounts have been produced in Imperial County.

*Ceramics.* Finely ground (about 98 percent through 200-mesh sieve) iron-free quartz, in proportions ranging from about 5 to 25 percent, is used in the bodies of whiteware, earthenware, chinaware, glazed wall tile, sanitary ware, and in glazes. Most of the quartz used for these purposes in California is pulverized vein quartz from Oklahoma and Arizona, but silica flour from Ottawa, Illinois, and from the Pacific Grove and Trabuco Canyon areas is also used. Specifications generally require a silica content of 95 to 99.8 percent, iron content of 0.05 percent maximum, and little or no feldspar, clay, soda or potash, depending on the usage.

*Soluble Silicates.* A special use of flint glass quality sands is in the soluble silicate industry. Sodium silicate, "water glass," of more than a dozen grades is produced in California. It is made by fusing silica sand and sodium carbonate, then dissolving the resulting material in water. It is sold mostly as an aqueous colloidal solu-







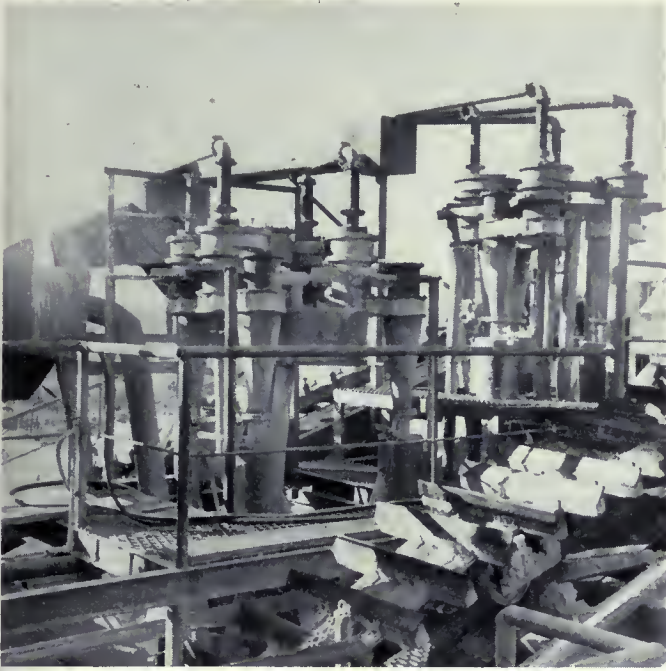


FIGURE 15. Krebs liquid cyclones installed at the plant of Crystal Silica Company at Oceanside. Sand is separated from clay by centrifugal action in these machines. (Photo courtesy of Equipment Engineers, Inc.)

pecifically for such purposes, sand is commonly obtained from established deposits and producers.

Minor amounts of specialty sand are used in California in aquariums, playground sandboxes, golf course sand

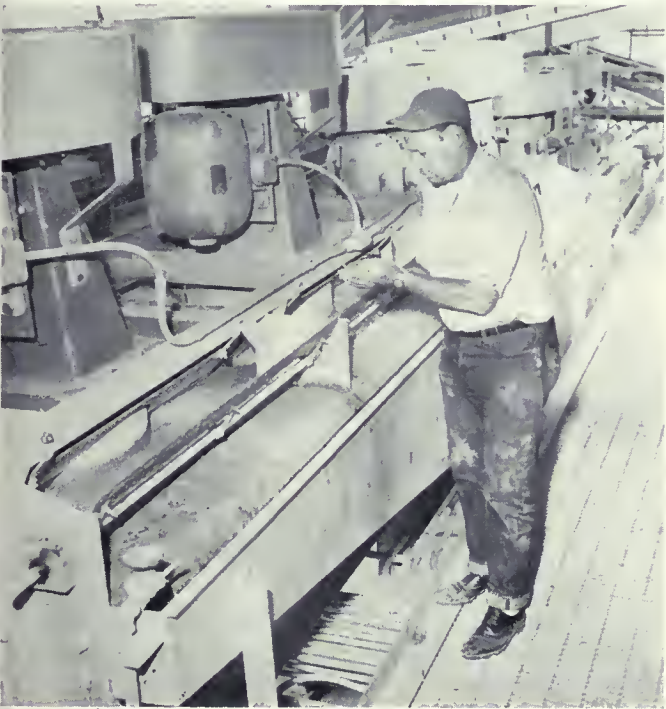


FIGURE 16. Flotation cells at Owens-Illinois glass sand plant at Ione, Amador County. Iron-bearing, and other heavy minerals float in surface froth and are brushed by paddles into trough at right side of tank for removal. Pure quartz sand sinks to bottom of tank for collection. (Photo courtesy of Owens-Illinois).

traps, cigarette urns, prepared and built-up roofing; as fire or furnace sand for lining metal smelting furnaces; as placing (potters) sand to support ceramic ware and to seal kilns during firing; as nursery or greenhouse gravel; and as special aggregate for concrete pipe linings. Minor amounts of silica flour are also used as filler in such materials as paint, paste wood filler, hard rubber, stucco plaster, gypsum plaster board, asphaltic mixtures, and special cements; and to provide dust baths for chin-chillas.

#### TREATMENT

Much of the specialty sand produced in California is marketed with little or no treatment (table 1). The principal groups of untreated special sands are: (1) naturally bonded foundry sands, obtained in many localities, (2) ganister, obtained in the Tesla and Trabuco Canyon areas, and (3) beach and dune sands, obtained in the El Segundo, Oceano Beach, and Monterey Bay areas and mainly used as sandblasting sand, engine sand, and clay-free foundry sand. Except for removal of gross organic debris, disintegration of large lumps, and sun-drying, most of these sands are used just as quarried. Certain operators kiln-dry, wash, and/or screen portions of their output of the El Segundo and Monterey Bay sands in wet weather or for certain uses.

Relatively complex sand treatment processes are required at the several localities where glass sand is produced in California, (1) to separate clay, (2) to reduce iron content to a minimum, and (3) to remove heavy minerals. Clay separation is effected in liquid cyclones, by rake and screw type classifiers, or by decantation in settling basins.



FIGURE 17. Overhead bins for loading engine sand into sand chambers of locomotives at Roseville yard of Southern Pacific Railroad Company, Sacramento County.

Iron present as limonitic coatings on sand grains is removed by vigorous beating of the sand as a high-solids slurry in attrition scrubbers. Iron present as ferruginous mineral grains is removed, as are other heavy minerals, by the use of concentrating tables, magnetic separators, or flotation cells.

Post-war development of liquid cyclones, attrition scrubbers, and flotation techniques have enabled large-scale production of high-purity glass sand. These newly developed methods also have permitted the recovery of



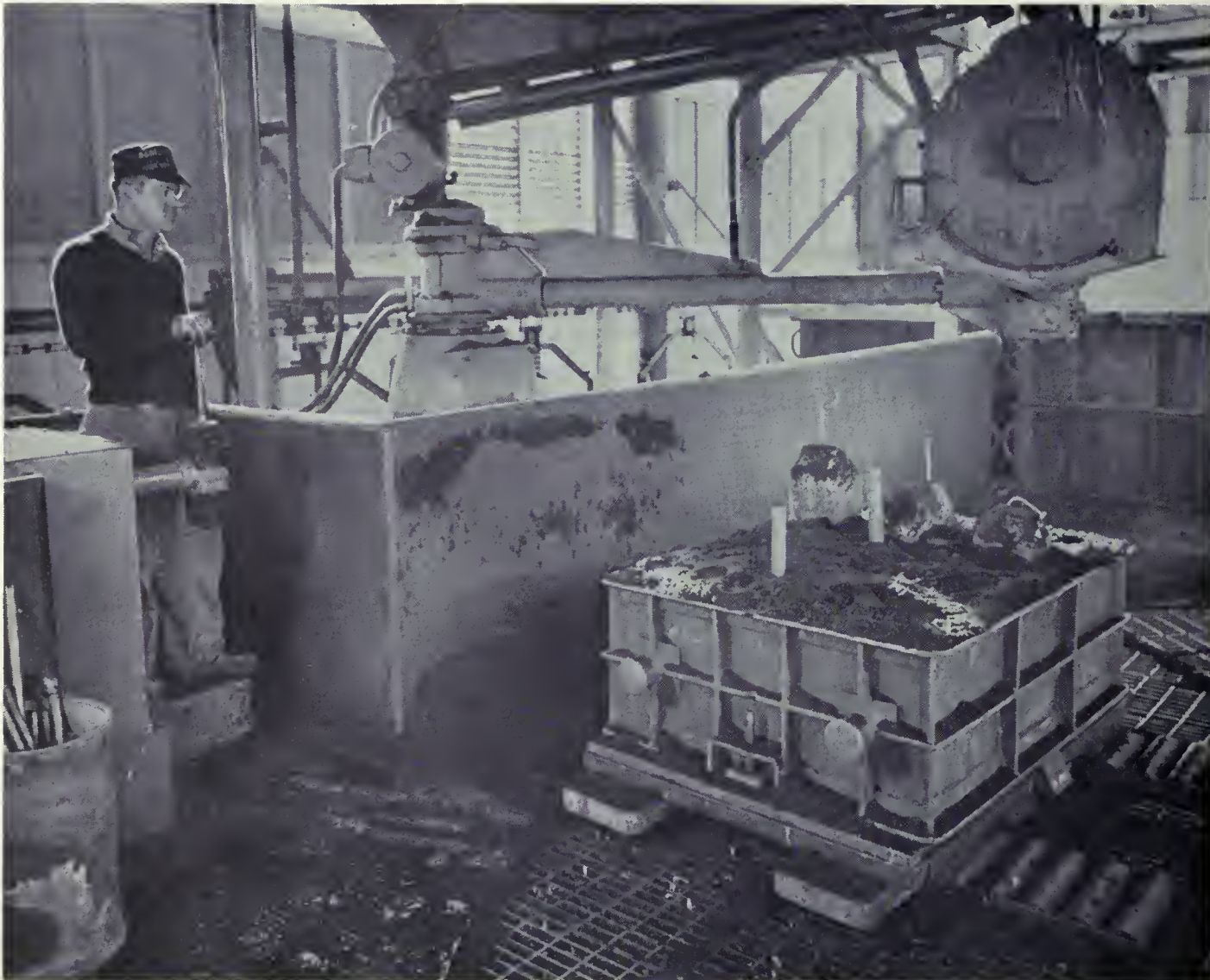


FIGURE 18A. Preparing a light sand mold on a molding turntable at the General Metals Corporation Oakland foundry. Operator controls position of the delivery head (right) of the sand-slinging machine as it distributes and rams sand in the mold. (Photo courtesy of General Metals Corporation).

high-quality glass sand from many large deposits whose high content of clay, or of iron-bearing minerals, had previously rendered them unsuited to this use.

California's principal sand-treatment plants are located near the deposits at Corona, Pacific Grove (two plants), Ione, Camanche, and Oceanside. The flowsheets of these plants differ because of differences in the types and proportions of impurities in the several deposits.

The Corona deposit contains excessive clay and fine material, as well as excessive iron both as sand grain coatings and ferruginous minerals. The Owens-Illinois Corona plant, which was enlarged and modernized in 1947, utilizes classifiers to remove loose clay. Iron oxide and clay coatings are removed from the quartz grains by attrition scrubbers and washed away in classifiers. Heavy minerals, in part iron-bearing, are removed by magnetic separators from the dried sand.

The Pacific Grove deposit contains little clay in the natural sand; iron is present as sand grain coatings, and

in ferruginous minerals. In 1952, the Del Monte Properties Company plant at Pacific Grove was redesigned to include attrition scrubbers to remove ferruginous sand grain coatings, and a flotation circuit to remove iron-bearing and other heavy minerals. A flotation circuit was also installed to separate the sand into pure quartz and pure feldspar components. A minor proportion of the output of pure quartz sand is ground in pebble mills to make silica flour. The Owens-Illinois Pacific Grove plant processes sand from the same deposit as the Del Monte Properties Company, but employs magnetic separators to discard iron-bearing and other heavy minerals.

Sand from the Ione formation, treated in the Owens-Illinois Ione plant and the Pacific Clay Products Camanche plant, contains a high proportion of valuable clay as well as iron sand grain coatings and ferruginous heavy minerals. The Owens-Illinois plant, placed in production in 1955 after two years of pilot plant tests, and the Pacific Clay Products plant, scheduled for completion in





FIGURE 18B. Hand pouring molten stainless steel into sand molds in the General Metals Corporation Oakland foundry. An induction furnace is in the background. (Photo courtesy of General Mills Corporation).

1956, utilize somewhat similar flowsheets. Liquid cyclones are used to remove most of the clay; classifiers remove the remainder. Iron-bearing and other heavy minerals are removed by flotation. The Pacific Clay Products plant also has attrition scrubbers, to remove coatings from the sand grains, and magnetic separators to further reduce the iron content.

The Tejon sand, utilized by the Crystal Silica Company plant at Oceanside, contains excessive clay, but is comparatively lacking in iron content. Liquid cyclones are used to discard clay, and in part to remove iron by attrition.

In the Trabuco Canyon area, the raw material is so rich in valuable clay, that silica sand is of byproduct importance. The sand and clay are separated primarily by decantation in shallow settling basins. The sand is further cleaned of clay by washing, and of iron by magnetic separators.

#### MARKETING AND PRICES \*

The relatively unprocessed types of specialty sand, such as naturally bonded foundry sand and untreated dune sand used for sandblasting and engine sand, are commonly sold in bulk, in truckload or carload quantities. Dune sand for use as engine sand ranges in price from about \$0.75 to \$2.00 per ton, f.o.b. deposits, in carload lots. Dune sand to be used for sandblasting is priced from \$1 to \$3 per ton, f.o.b. plants, and \$2 to \$6 delivered in truckload lots. Naturally bonded foundry sand costs from \$5.50 to \$10 per ton delivered in the Los Angeles area; transportation costs add about \$6 to the delivered price in the San Francisco Bay area. Ganister costs \$10 to \$13 per ton delivered in the Los Angeles and San Francisco areas.

Filter sand and gravel is the only type of specialty sand that is commonly sold by the sack. Hundred-pound

\* Price data obtained in 1955.





FIGURE 19. Sewage treatment plant at Barstow, San Bernardino County, showing filter gravel used as trickling medium. Diameter of tank is about 100 feet.

(1 cubic foot) sacks are sold for 60 to 70 cents each, f.o.b. yards, and as much as \$1.50 delivered in the Los Angeles area. In bulk filter sand is sold for about \$14 per ton and filter gravel for \$8 or more per ton, in truckload lots, f.o.b. plants in southern California. Prices for the sand used in municipal filter plants are somewhat lower, but are not available for publication. Well-packing gravel is sold for about \$14 per ton in bulk, f.o.b. plant, in the Los Angeles area.

Processed sands, suitable for glass manufacture, filter sand, or clay-free foundry sand, are sold within the general range of \$4 to \$7 per ton f.o.b. plants in California. Prices vary with such factors as grade of sand, size of order, whether shipped in bulk or in sacks, and whether shipped wet or dry. Processed Nevada sand, suitable for glass and foundry usage, is sold for about \$2 to \$6 per ton f.o.b. Lake Mead. It is transported by rail to the Los Angeles area for about \$3.50, and to the San Francisco area for about \$5 per ton. Sand from Ottawa, Illinois, costs about \$3 to \$5 per ton, f.o.b. Ottawa, and about \$15 to \$18 per ton delivered in carload lots in Los Angeles.

Silica flour, approximately 95 percent smaller than 200 mesh, from Ottawa costs \$20 per ton (bulk) and \$23 (sacked) delivered in Los Angeles. Sacked silica flour from Pacific Grove costs about \$15 per ton f.o.b. plant, and about \$19 per ton delivered in Los Angeles.

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## STONE, CRUSHED AND BROKEN

By THOMAS E. GAY, JR.

Stone production is one of the oldest and most extensive mineral industries in California. Before the early nineteen hundreds, dimension stone was produced in the state in much greater volume than crushed stone. During the past 50 years the output of dimension stone has dwindled, while the production of crushed stone has increased many fold. Greatly increased use of crushed stone for aggregate, especially in asphalt concrete for paving, and the marked decrease in use of dimension stone for building stone, paving blocks, or curbing is largely responsible for this trend.

In 1952, California ranked seventh, among the states, in stone production with a total output of approximately 14,374,930 short tons, valued at \$17,697,085 (Bowles and Jensen, 1955, p. 3). Of this total only 46,707 tons, or about 0.03 percent, was dimension stone. Crushed stone ranked in value only behind petroleum products, cement, and sand and gravel among California's mineral commodities. Thirty-two of the state's counties reported production of stone in 1953, although an undetermined number of other counties also yielded crushed stone and reported it as sand and gravel.

### TERMINOLOGY

Although the terms "rock" and "stone" commonly are used synonymously, they have different meanings when strictly applied. "Rock" has been defined variously by geologists, but in the stone industry it is applied to any mass of mineral aggregate as it exists in its natural state and in place. "Stone" refers to individual blocks, masses, or fragments that have been broken or quarried from bedrock exposures, or obtained from boulders and cobbles in alluvium, and that are intended for commercial use. Natural mixtures of alluvial sand and gravel constitute a type of rock, but in this volume are discussed mainly in the sections on sand and gravel, and specialty sands.

Most deposits of economic minerals have formed under relatively uncommon geologic conditions, but stone is obtained from the ordinary rocks that constitute the earth's crust. The materials that can be classed as stone are numerous, widespread, and of a wide range of geologic ages and modes of origin.

Stone has many industrial applications, but these can be divided into two general classifications by usage: (1) crushed and broken stone, and (2) dimension stone. Crushed and broken stone includes all stone in which the shape is not specified, such as that used as aggregate, railroad ballast, and riprap. Dimension stone is produced to specified dimensions, and includes stone employed as building stone, monumental stone, curbing, and flagstone (see section on dimension stone in this volume).

For most uses crushed or broken stone should be durable, dense, sound, hard, strong, able to withstand high temperatures, and tend to break into suitably shaped fragments. In almost all uses stone must resist the chemical action of weathering. Stone used in coastal installations must also resist chemical action of seawater; common aggregate must contain little or no potentially reactive material; aggregate for use in acid-resistant con-

crete must be especially stable chemically. Moreover, stone to be used for certain special purposes such as the limestone used in agriculture, glass manufacture, or the sugar refining industry, must be chemically suited to these applications.

Crushed and broken stone is commonly further subdivided, on the basis of use, into (1) crushed stone, (2) riprap, (3) furnace flux, (4) refractory stone, (5) agricultural stone, and (6) stone used for other purposes (Bowles and Jensen, 1955). Crushed stone is mainly used as aggregate in asphalt concrete for paving purposes, railroad ballast, aggregate in portland cement concrete used for various construction purposes, aggregate base, and fill. Riprap consists of large broken stone used without a binder, principally for jetties, breakwaters, and sea walls which are intended primarily to resist the physical action of water. Furnace flux consists of limestone and marble used for chemical purposes in the refining of iron ores and in other metallurgical practices. Refractory stone includes quartzite, mica schist, dolomite, and soapstone which are used in the manufacture of refractory brick, and for furnace and ladle linings. Agricultural stone includes any type of stone that is added to soil, either as a fertilizer or a soil-conditioner. The category "other purposes," includes crushed stone used as a filler, poultry grit, roofing granules, stone sand, and terrazzo granules; and in the production of mineral wool, stucco, artificial stone, and mineral food; in coal mine dusting; and for various chemical applications.

Many materials that by definition can be classified as stone are considered as separate commodities. Dolomite, limestone, vein quartz and quartzite, sand and gravel, and specialty sands, as well as such stone-like nonmetallic materials as diatomite, pumice, perlite, volcanic cinders, and soapstone are described more completely elsewhere in this volume.

### ROCKS USED AS CRUSHED AND BROKEN STONE IN CALIFORNIA

The stone industry recognizes the following stone classification based mainly on composition and texture: (1) granite; (2) basalt and related rocks; (3) limestone; (4) marble; (5) sandstone; and (6) miscellaneous stone (including chert, conglomerate, greenstone, serpentine, shale, slate, mica schist, tuffaceous volcanic rocks, and volcanic cinders). Most of these types are abundant and widespread in California, both in bedrock outcrops ("basement rock") and as fragments in alluvial deposits. The alluvial deposits, which are mostly of Quaternary age, yield stone as a co-product of sand and gravel operations in which oversize cobbles and boulders are crushed and sold separately. Minor tonnages of stone from alluvial deposits are used as rustic building stone, and as dam facing cobbles.

*Granitic Rocks.* The term "granite" is commonly applied to medium- to coarse-grained igneous rocks that consist mainly of feldspar and quartz, and ordinarily contain subordinate proportions of ferromagnesian minerals. In the stone industry, and in the following dis-



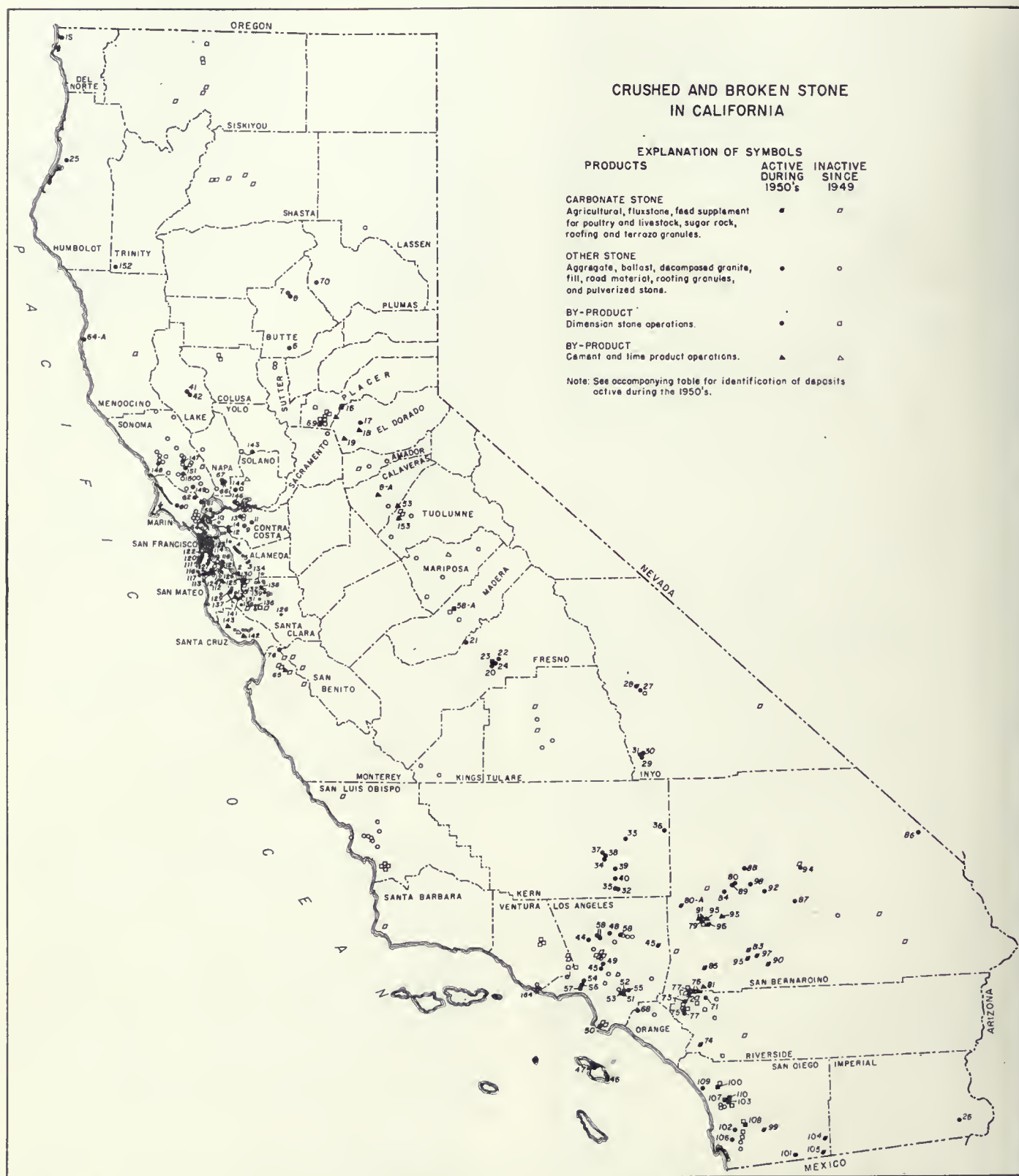


FIGURE 1. Map showing locations of crushed and broken stone operations in California, including dimension stone and carbonate stone quarries that have yielded crushed stone as a byproduct. From U.S. Bureau of Mines and California Division of Mines records.



*List of crushed and broken stone operations in California active during the 1950's; for locations see accompanying map p. 566*

ALAMEDA CO. 1. Gallagher and Burke, Inc. 2. Leslie Salt Co. 3. Niles Quarry Co. 4. San Leandro Rock Co. 5. Sorum and Gendreau	28. Inyo Marble Co. 29. Redlite Aggregate, Inc., volcanic cinders 30. Paul R. Splane Co., volcanic cinders 31. Volcanic Cinder Co., volcanic cinders	MARIN CO. 59. Basalt Rock Co. 60. Black Mountain 61. Black Point Aggregates Inc. 62. Burdell Mountain 63. Forbes 64. Greenbrae Quarries	85. Industrial Roofing Rock Co. 86. Ivanpah Silica Quarry 87. Mt. Pisgah volcanic cinders 88. Painted Desert Co. 89. Rainbow Rock Inc. 90. Rattlesnake Gulch Deposit	122. Pacific Coast Aggregates, Brisbane 123. Sanitary Fill 124. Skyline Materials Inc. 125. Peter Sorenson 126. Tyson 127. W.P.A.
BUTTE CO. 6. Henry J. Kaiser Co. 7. Kemen 8. Sake and Saunders	32. Desert Rock Milling Co. (mill) 33. Groover Mining & Milling Co. (mill) 34. Hidecker Rock Co., Horse Canyon (mill) 35. Hidecker Rock Co., Rosamond (mill) 36. Higham (mill) 37. M & M Milling Co. (mill) 38. McLaughlin, Zenor and Mamey (mill) 39. Mojave Mineral Products Co. (mill) 40. Mojave Rock Products Co. Inc. (mill)	MENDOCINO CO. 64A. Noyo Harbor riprap quarry	91. Riverside Cement Co. 92. Sharp and Fellows Construction Co. 93. Southwestern Portland Cement Co. 94. Union Pacific Railroad Co. 95. Van Dusen Canyon Deposits 96. Victorville Lime Rock Co. 97. White Rock Limestone quarry 98. Tom Woolsey (mill)	SANTA CLARA CO. 128. Anderson Lake 129. Bahr and Ledoyen 130. Bay Shell Co. 131. Commercial Materials 132. County Alum Rock 133. County Saratoga 134. Frederickson-Watson 135. R. G. Gambetta, shells 136. Mirasson Bros. 137. Permanente Cement Co. 138. Piazza 139. Roggach Bros. 140. Sondgrath Bros. 141. A. F. Voss
CALAVERAS CO. 8A. Calaveras Cement Co.		MONTEREY CO. 65. Kaiser Aluminum and Chemical Corp.		
CONTRA COSTA CO. 9. N. M. Ball Sons 10. Blake Brothers 11. Harrison-Birdwell 12. Henry J. Kaiser Co. 13. Serra Bros. 14. Tunnel Rock Quarry		NAPA CO. 66. Basalt Rock Co. 67. Juarez Quarry		
DEL NORTE CO. 15. Rowdy Creek Crusher Co.		ORANGE CO. 68. D. D. Lawhead and Sons		
EL DORADO CO. 16. California Rock and Gravel Co. 17. Pacific Minerals Co., slate 18. Diamond Springs Lime Co. 19. El Dorado Limestone Co.	LAKE CO. 41. Aggrellite Co. 42. Coleman Quarry	PLUMAS CO. 70. Western Pacific Railroad Co.	SAN DIEGO CO. 99. Alpine Roof Granules 100. California Cui Stone 101. Campo Milling Co. 102. Canyon Rock Co. 103. Escondido Quarries Inc. 104. Heathman 105. Jacumba Roof Granules 106. Mission Gorge Quarry 107. National Quarries 108. Southern California Granite Co. 109. J. B. Stringfellow Construction Co. 110. Valley Granite Co.	SANTA CRUZ CO. 142. Pacific Limestone Products Co. 143. Santa Cruz Portland Cement Co.
FRESNO CO. 20. Atchison, Trepeka and Santa Fe Railway Co. 21. County decomposed granite pit 22. Sharp and Fellows Construction Co. 23. Superior-Academy Granite Co. 24. Tivy Valley decomposed granite pit	LOS ANGELES CO. 43. Amercal Mining Co. 44. Blue Cloud Chinchilla Dust 45. W. J. Bonfield 46. Connolly-Pacific Co. 47. Graham Bros., Inc. 48. Katz (Boiling Point) soapstone 49. Katz (Schwartz Canyon) shale 50. Livingston Rock and Gravel Co. 51. Los Angeles Decomposed Granite Co. 52. McCaslin Materials Co. 53. Monterey Park Granite Co. 54. Mulholland DG Co. 55. Owl Rock Products Co. 56. Santa Ynez Canyon limestone 57. Santa Ynez Canyon sandstone 58. Sierra Pelona Rock Co.	RIVERSIDE CO. 71. Atchison, Trepeka and Santa Fe Railway Co. 72. Haven Granite Co. 73. Livingston Rock and Gravel Co. 74. Lucas Mining Co. 75. Minnesota Mining and Manufacturing Co. 76. Riverside Cement Co. 77. J. B. Stringfellow Construction Co.	104. Heathman 105. Jacumba Roof Granules 106. Mission Gorge Quarry 107. National Quarries 108. Southern California Granite Co. 109. J. B. Stringfellow Construction Co. 110. Valley Granite Co.	SOLANO CO. 144. Cordelia Quarries 145. Fredrickson Bros. 146. Parish Bros.
HUMBOLDT CO. 25. Tom Hull		SAN BENITO CO. 78. Granite Rock Co., Logan	SAN MATEO CO. 111. California Aggregates 112. Canada Road, South 113. Canadas Quarry 114. Causeway 115. Edgewood Road 116. El Granada 117. Hilltop 118. Ideal Cement Co. 119. Macco-Morrison-Knudson Construction Co. 120. Marks Materials 121. North Road	SONOMA CO. 147. Construction Supply Co. 148. Thomas A. Graham 149. Hein Bros.—Basalt Rock Co. 150. Talbert Rock Quarry 151. Zaney Gravels Co.
IMPERIAL CO. 26. Western Non-Metallies		SAN BERNARDINO CO. 79. Atlas Silica Quarry 80. Brubaker-Mann Co. 80A. California Dolomite Co. 81. California Portland Cement Co. 82. Chubbuck Deposits 83. Cushenbury Canyon Quarry 84. Stuart Ingram Co.		TRINITY CO. 152. Northwestern Pacific Railroad Co.
INYO CO. 27. Gladding McBean and Co.	MADERA CO. 58A. Raymond Granite Quarries			TUOLUMNE CO. 153. U. S. Lime Products Co.
				VENTURA CO. 154. J. B. Stringfellow Construction Co. 155. Western Lime Products Co.

cussion, the terms "granite" and "granitic rock" are used even more broadly to refer to various intrusive igneous rocks with granitoid textures, and to some metamorphic rocks with gneissic textures.

Most unweathered granitic rocks are hard, strong, tough, and resistant to abrasion, impact, and chemical attack. These properties make granitic rock well suited to use as building stone, riprap and aggregate. Granitic rock that is attractive in appearance and can be polished is commonly quarried for use as building and ornamental stone (see section on dimension stone).

Granitic rocks occur mainly in large bodies, known as batholiths, which are exposed over many square miles. In California granitic rocks occur mostly in the Sierra Nevada and Southern California batholiths and in smaller masses in the Klamath Mountains and the desert regions of eastern and southern California. These bodies together underlie about 40 percent of the state's area and are largely or wholly of Mesozoic age. Batholiths commonly consist of numerous individual bodies of various granitic rock types, with contrasting colors, textures, and mineral composition. The two great batholiths of California are exposed mostly in mountainous areas, but the main granite quarries lie about their peripheries or in outlying smaller masses, so that the quarries are as close as possible to major transportation routes to centers of consumption. Over wide areas of the state the exposed granitic rocks are so deeply weathered or highly fractured as to be unsuited to the purposes outlined above. In the Los Angeles area, for example, little or none of the granitic rock exposed in the nearby Santa Monica or San Gabriel Mountains is sufficiently unshattered or unweathered to be quarried as crushed stone in large tonnages. With the exception of the crushed stone recovered in sand and gravel operations, all granitic stone must be brought to the Los Angeles area from quarries in Riverside, San Diego and San Bernardino Counties, 45 to 100 miles away. Disintegrated and shattered granitic rock, known commercially as decomposed granite, or "DG," is much used in southern California as aggregate base, low-quality paving material, and fill.

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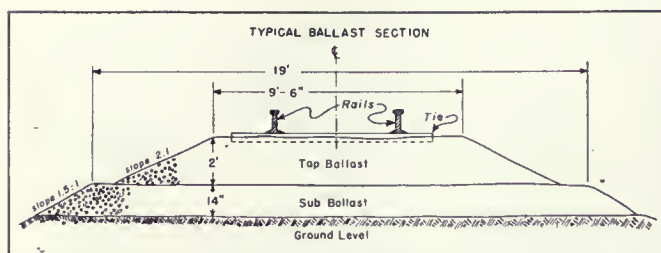


FIGURE 2. Cross section through typical standard gauge railroad track, showing position of rails, ties, and ballast. Depth and width of ballast differ according to the location and expected use of the track, but commonly remain within the limits shown. After Smith, 1956, p. 6, figure 5.

In California, granitic rock has been quarried mainly for use as dimension stone and riprap, but the quarry waste has been a source of crushed stone for local uses. These quarries lie mainly in (1) the western foothills of the Sierra Nevada, in the western part of the Sierra Nevada batholith, and (2) along the western and northern borders of the Southern California batholith. In the San Francisco Bay area, granite quarries have yielded crushed and broken stone from Montara granite in San Mateo County, and from Franciscan diorite-gabbro in Santa Clara County.

The principal granite quarries in California are near Raymond, Madera County; Folsom, Sacramento County; Penryn, Loomis, and Rocklin, Placer County; Logan, San Benito County; the Jurupa Mountains and vicinity, Riverside and San Bernardino Counties; and near Lakeside, Escondido, and Vista, San Diego County. Of these quarries, all except the Logan quarry, and several near Riverside have been primarily dimension stone operations.

**Decomposed Granite.** Weathering may decompose the feldspar and ferromagnesian minerals in granitic rock,

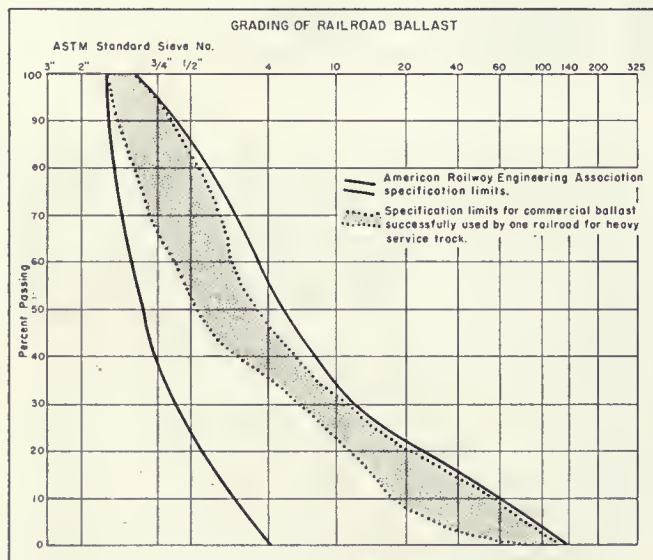


FIGURE 3. Particle size distribution curves showing size limits specified for sand and gravel ballast (a) by American Railway Engineering Association for all ballast, and (b) by one railroad company for commercial ballast that proved successful in use. To be acceptable as ballast, the size distribution curve of the material must lie within the limits shown. After Smith, 1956, p. 7, figure 6.

and convert once-sound rock in situ to a weak, relatively friable mass of quartz grains, clay and partially decomposed grains of feldspar and ferromagnesian minerals. Granite that has been shattered by fault action is particularly susceptible to decomposition by weathering. Weathering in sedimentary deposits of granitic debris may render the stone unsound for use as aggregate and if sufficiently advanced, convert the deposit to the equivalent of decomposed granite.

Decomposed granite ordinarily can be loosened and quarried by power shovel or bulldozer, without blasting. Crushing and screening are commonly unnecessary.

Decomposed granite is valued for sub-grade, road base, and fill because it is easy to handle, packs and holds well, has sufficient bearing strength and stability under load, and allows adequate drainage. Its widespread availability at low cost is another reason for its extensive use. For the uses mentioned, decomposed granite is preferred both to earth and to sand and gravel, either of which may be used when decomposed granite is unavailable.

As an extremely low-cost material employed in relatively non-exacting uses, decomposed granite can rarely be economically hauled farther than a few miles to the site of use. Therefore it is used extensively only in those sections of California where it occurs near metropolitan areas, especially the Los Angeles area.

**Basalt and Related Rocks.** In commercial usage, and in this discussion, the term "basalt" is applied to any of the dense, fine-grained, dark-gray or black volcanic rocks. The term ordinarily includes rock types that geologists classify as dacite, andesite, basalt, trachyte, or latite. Basaltic rock has solidified by the cooling of lava, either as flows on the earth's surface, or as shallow intrusive bodies beneath the surface. It is composed primarily of feldspar and ferromagnesian minerals in crystals that range in size from submicroscopic to clearly visible. Commonly an appreciable percentage of glassy material is present. Some effusive basalt is vesicular and the vesicles may have become filled with potentially reactive substances such as opaline silica or zeolites which render the rock unfit for use as aggregate.

Basaltic rocks are characteristically hard, tough, and durable, so are best suited for use as aggregate, railroad ballast, and riprap. Some types of crushed basaltic rock are well suited for use as artificially colored roofing granules. In the past, much of the basalt quarried in California was used as paving blocks, especially in industrial areas and steep hills where strong resistance to shock and abrasion are desired, but in recent years concrete paving mixtures have almost completely replaced it in this use. The once-important but now rare usage of tuffaceous volcanic stone for building and paving purposes is discussed in the chapter on dimension stone, in this volume.

Basaltic rocks are extensively exposed in many localities in California. In the northeastern part of the state Tertiary and Quaternary basaltic rocks are exposed for hundreds of square miles in the Modoc Plateau and form the most extensive occurrences. A number of smaller areas, measurable in tens of square miles or less, occur scattered in the Sierra Nevada and Mojave Desert provinces in the northeastern portion of central and southern California. Little basaltic stone is obtained





FIGURE 4. Photo showing one of the largest of California's crushed stone operations, Granite Rock Company, at Logan, San Benito County. Pre-Franciscan Santa Lucia granitic rock, much shattered by movement along a branch of the San Andreas fault which trends along the railroad at left, has been obtained here since 1900. A hill that formerly extended more than 400 feet above the present quarry floor has been removed. The lower working face is about 100 feet high, the upper one ranges up to 200 feet in height. Photo taken 1955.

from these areas because of their remoteness from the main centers of use, but some has been quarried for local construction projects and for railroad ballast.

Less extensive occurrences in the Coast and Peninsular Ranges are the sources of most of the basaltic stone produced in the state. Basaltic rock, largely altered to "greenstone," is abundant in the Franciscan formation, and in various Tertiary formations in the Coast Ranges. In the San Francisco Bay area, where alluvial sand and gravel must be hauled long distances, basaltic rock has been quarried and crushed for portland cement and asphalt concrete aggregate especially north of the Bay, in Marin, Sonoma, Napa, and Solano Counties. Basaltic stone for paving stone and curbing was once extensively produced at a score or more of deposits in that area, but portland cement concrete has largely replaced stone for this use, and nearly all of these deposits are idle. Notable quantities of basaltic stone also have been produced near Orinda, Contra Costa County; Newberry, San Bernardino County; Corona, Riverside County; Palos Verdes Hills and Santa Catalina Island, Los Angeles County; and Arcata and Trinidad, Humboldt County.

**Carbonate Rock—Limestone and Marble.** Carbonate rocks are abundant and commercially important in California. (see sections on lime, limestone, and dolomite, and cement). Carbonate rocks are broadly divided by geologists into 1) limestone, which consists almost entirely of calcite ( $\text{CaCO}_3$ ); 2) dolomite, which consists mainly of the mineral dolomite ( $\text{CaCO}_3 \cdot \text{MgCO}_3$ ); and 3) marble, which is the metamorphosed crystalline equivalent of either type. All gradations exist between limestone and dolomite and between very fine-grained and very coarse-grained material. Virtually all of the carbonate rock that is marketed as crushed stone was originally deposited as a marine sediment.

In the stone industry the term limestone is applied to many types of rock that contain a high percentage of calcium carbonate, although large proportions of other substances also may be present. Such substances include

dolomite, siderite ( $\text{FeCO}_3$ ), magnesite ( $\text{MgCO}_3$ ), and rhodochrosite ( $\text{MnCO}_3$ ). They also commonly contain clay, silt, and sand grains. A high percentage of clay commonly weakens carbonate rock, and makes it unfit for use as stone; a high content of sand grains or silica may make carbonate rock too hard to be prepared for use economically.

In the stone industry the term "marble" is applied to any carbonate rock that will take a high polish and includes various dense types of limestone and dolomite. The term is also loosely applied to coarsely crystalline carbonate rocks. The classification of carbonate rock either as limestone or marble therefore is determined largely by its use. Stone from many California deposits, for example, has been used both as limestone (e.g. in the sugar industry) and as marble. Nearly all of the crushed carbonate stone produced in California is classified as limestone.



FIGURE 5. Photo showing one of California's many small crushed stone operations, along Highway 1 south of Mendocino, Mendocino County. Contorted, brecciated Franciscan (?) sandstone is crushed in small portable plant intermittently as needed for road material. Photo taken 1955.





FIGURE 6. Photo showing quarry of Guy F. Atkinson Company, north of Brisbane, San Mateo County, where Jurassic Franciscan sandstone has been obtained since 1954 for use as fill. Truck-borne drill on upper bench drills 30-foot blast holes. Five-yard power shovel loads 20-yard trucks for haul to fill sites; production about 13,000 cubic yards per day. *Photo by Fenelon F. Davis, 1954.*

For use as stone, carbonate rock should be physically sound, dense, and relatively pure. Carbonate stone that is strong, tough, and durable is well suited for use as concrete aggregate, road metal, railroad ballast, and riprap. A pure white color also is desirable in carbonate stone to be used for granules in built-up roofing, and various colors are desirable in granules to be used for terrazzo.

Most of the carbonate stone produced in California in recent years has been used primarily for its chemical properties, and has been consumed in the cement, lime, agricultural, and various other process industries. Relatively small tonnages have been produced for use as crushed and broken stone, or as dimension stone.

Finely pulverized carbonate rock (which is used extensively as a soil additive, ceramic ingredient, a chemical, and for filler and whiting) as well as crushed limestone (which is used as fluxstone, sugar rock, and in glass manufacture) are discussed in the section on lime, limestone and dolomite in this volume. Relatively little has been used as aggregate, railroad ballast, fill, or riprap in California although such uses of carbonate rock are common in other states. Several thousand tons of crushed carbonate stone are used each year in California for roofing granules, poultry feed supplement, and terrazzo.

Occurrences of carbonate rocks are extensive and widespread in California (see section on lime, limestone, and dolomite in this volume; also Logan, 1947, pp. 201-350). Deposits are especially numerous in the western Sierra Nevada province, the northeastern portion of the Klamath Mountains province, the Great Basin, Mojave Desert, and Colorado Desert provinces in southeastern California; in the Coast Ranges, mainly south of San Francisco, and in the Peninsular and Transverse Range provinces of southern California. The ages of these deposits range from Miocene to pre-Cambrian.

From locality to locality and even within many individual deposits both the physical and chemical qualities of carbonate rocks differ greatly. Except in the desert areas of eastern California where exposures several

square miles in area are common, most of the occurrences cover 10 acres or less. Deformation and various degrees of recrystallization are common in the carbonate rocks throughout the state.

Many deposits of carbonate rock physically and chemically suited to use as stone have not been quarried because they are (1) inaccessible to large machinery, (2) too distant from market areas for economic haulage, especially in northern and eastern California, or (3) reserves are too small to warrant the investment needed to open a quarry. Many deposits quite close to market areas remain unquarried because of quality deficiencies. At 300 or more localities in 47 counties deposits of carbonate stone have been quarried in California (Logan, 1947). Most of these were very small operations which were active only in the late 1800's and early 1900's, and were sources of limestone which was burned to lime and used locally. Since the early 1900's quarries

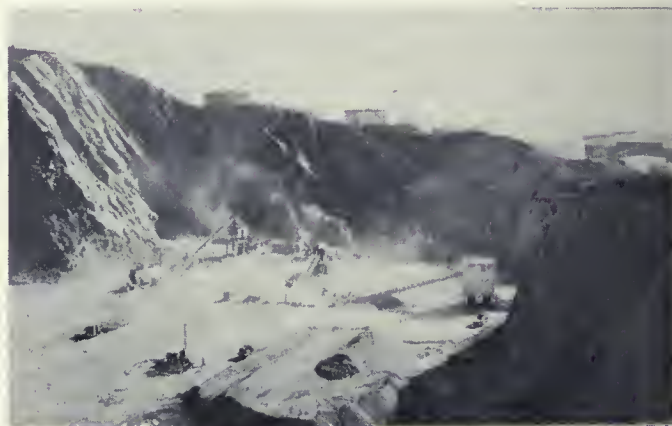


FIGURE 7. Photo showing Blake Brothers quarry, Point Richmond, Contra Costa County, where steeply dipping Franciscan sandstone has been obtained for aggregate and riprap since 1907. Circular quarry amphitheatre is about 1000 feet in diameter, with working face (off photo, left) about 400 feet high. Photo taken 1955.



in several districts have yielded substantial tonnages of dimension stone, and a minor but undetermined proportion of crushed and broken stone as a by-product. The cessation of local lime-burning operations has been caused largely by the great increase in production and use of portland cement.

Although minor quantities of crushed carbonate stone have been produced at numerous localities in the state, especially for use as roofing granules, only two areas have yielded crushed and broken carbonate rock, on a continuing basis, for use as riprap, aggregate, road base, or railroad ballast. One is in San Mateo County, where four quarries have been worked; and the other in Los Angeles County where one quarry exists. A score or more localities contain dimension stone quarries that have yielded crushed and broken limestone as a by-product (Aubury, 1906, pp. 61-114; Logan, 1947), but most of these are now inactive. Notable in this group are the dimension stone quarries near Columbia, Tuolumne County; Plymouth and Voleano, Amador County; San Andreas and Angels Camp, Calaveras County; and Keeler, Inyo County. Nearly all the cement, lime, and industrial limestone operations in the state market off-specification material as roof granules, white aggregate, and other relatively non-exacting purposes, rather than discard it.

**Sandstone.** Sandstone is elastic sedimentary rock composed of particles mainly in the size range of about one fourth to one hundredth of an inch in diameter. Some sandstones consist almost wholly of quartz grains, but most sandstones are feldspathic and some contain a high proportion of ferromagnesian minerals. The strength and durability of sandstone are mainly determined by the type of material that cements the grains together. Only well indurated sandstone, cemented with silica or calcite (rather than with the weaker cements, clay or iron oxide), is well suited to use as crushed and broken stone. Loosely consolidated sandstone, however, especially that rich in quartz grains, commonly is used as a source of aggregate sand or specialty sand (see sections on sand and gravel, and specialty sands in this volume).



FIGURE 8. Photo showing barge-loading facilities of Blake Brothers, at Point Richmond, Contra Costa County. Covered belt conveyor from crushing plant (off photo, left) and stiff-leg clamshells load crushed Franciscan sandstone aggregate on barges for delivery throughout the Bay area. San Francisco is on skyline at right; foundations for Richmond-San Rafael bridge in foreground. Photo taken 1953.



FIGURE 9. Photo showing crushing and screening equipment, and stockpiles of Harrison-Birdwell Company, near Clayton, Contra Costa County, where Franciscan sandstone has been obtained since 1947, mainly for drainrock and road material. Photo taken 1953.

Most of the sandstone that occurs in California is very friable, but some is sufficiently durable to be used for riprap, railroad ballast, portland cement, concrete aggregate, and bituminous-bound concrete aggregate.

Virtually all of the sandstone in California occurs in formations that lie within the age range of Jurassic to Quaternary. Commonly, the older sandstones are harder and stronger than the younger ones, hence are better suited to use as crushed and broken stone.

Sandstone is extensively exposed in most of the western and central parts of the state, but sandstone for use as crushed and broken stone has been produced mainly in the San Francisco Bay area where the scarcity of sand and gravel has led to the abundant use of crushed stone for aggregate, ballast, and fill, as well as riprap in harbor projects.

#### MISCELLANEOUS TYPES OF ROCKS

**Chert.** Chert is a sedimentary rock composed almost entirely of silica, in the form of opal, chalcedony, or microgranular quartz. It commonly occurs in thin-bedded deposits.

In its most desirable form chert is a hard, dense, extremely durable stone. Such material is exceptionally well suited for use as crushed and broken stone aggregate in portland cement and asphalt concrete, railroad ballast and riprap. Some chert, however, is too laminated or contains too much silt or shale to be thus employed. Other chert deposits contain opaline silica which is reactive when used as portland cement concrete aggregate (see discussion of aggregate reactivity in section on sand and gravel in this volume). Recrystallized chert in metamorphic terranes is not reactive and makes excellent aggregate.

Chert deposits large enough to be quarried occur in the Franciscan formation which is widely distributed in the northern and central Coast Ranges. Such deposits also are contained in the Miocene Monterey formation which is widespread in the central and southern Coast Ranges, in the western Transverse Ranges, and the northern Peninsular Ranges.





FIGURE 10. Photo of Graham Bros., Inc., quarry near Empire Landing, Santa Catalina Island, Los Angeles County. The Mesozoic (?) serpentine obtained here is barged to the mainland for use as riprap and for harbor projects. Photo taken 1954.

In California the chert that has been used for crushed and broken stone has been produced mainly in the San Francisco Bay area. Franciscan chert, partly recrystallized, has been produced near Oakland and Niles, Alameda County; near San Rafael, Marin County; in San Francisco County; and near Belmont, San Mateo County. In at least one locality the Miocene Monterey formation has yielded chert for use as crushed and broken stone. This lies north of San Jose in Santa Clara County. Nearly all of these chert operations were idle in 1955.

**Conglomerate.** Conglomerate is elastic sedimentary rock containing abundant fragments of pebble size or larger in a matrix of sand and finer-grained materials. Conglomerates show various degrees of induration which depend largely on the nature and amount of cementing



FIGURE 11. Photo of Pebbly Beach quarry of Connolly-Pacific Company, Santa Catalina Island, Los Angeles County. Mesozoic (?) meta-conglomerate is obtained from a shelf nearly half a mile long, more than 100 yards wide, with working face more than 500 feet high. Riprap in pieces weighing as much as 35 tons is barged from here to the mainland for harbor projects. Note riprap blocks on flat quarry floor between camera and power shovel. Photo taken 1955.

material—clay, calcium carbonate, iron oxides or silica—in the matrix.

Conglomerate is not abundantly used in California for aggregate, riprap, or ballast because relatively few deposits of conglomerate near the main centers of use are sufficiently well indurated for these uses. When crushed, most of these conglomerates revert essentially to their sand and gravel components. Such deposits are quarried locally as sources of sand and gravel and for material to be used as road base materials, or fill. Highly weathered conglomerate is quarried in the Los Angeles area for use as decomposed granite.

In California, the principal source of conglomerate for use as crushed and broken stone is a body of well indurated conglomerate within the Mesozoic (?) Catalina schist at Pebbly Beach, Santa Catalina Island, Los Angeles County (figures 11, 12). This deposit has been worked for many years, and pieces weighing as much as 35 tons have been hauled by barge to the mainland. The quarried material has been used mainly as riprap and harbor stone in the Long Beach area. In the San Francisco Bay area conglomerate is quarried in a number of localities, principally for use as road material and fill.

**Greenstone.** Greenstone is a general term applied by geologists to basic or intermediate volcanic rocks that contain abundant green secondary minerals. In the stone industry the term is also applied to a variety of fine-grained green rocks, including arkosic sandstone, graywacke, impure quartzite and various pyroclastic rocks.

Rocks classifiable as greenstone in this broader sense are moderately abundant in many parts of California,



FIGURE 12. Photo showing barge-loading facilities at Pebbly Beach quarry of Connolly-Pacific Company, Santa Catalina Island, Los Angeles County. Fifteen-yard trucks back into metal skip (right) and dump broken stone. Thirty-ton stiff-leg crane lifts skip and empties contents into barges for tow haulage to mainland harbor project sites, mainly in the Long Beach area. Photo taken 1955.

but relatively small tonnages are used as crushed and broken stone. Many occurrences of greenstone are outside the range of economic haulage to main centers of use, and much of the more readily available greenstone is of inferior quality.

Much of the crushed greenstone is employed for uses in which a green color is specifically desired, such as for naturally colored roofing granules. Physically sound





FIGURE 13. Photo showing Declez quarry in the Jurupa Mountains near Declezville, San Bernardino County. Cretaceous Bonsall tonalite has been obtained here intermittently since prior to 1900; mainly for railroad and breakwater riprap, with minor output for dimension stone. The quarry face has total length of more than 2,000 feet, and maximum height of about 100 feet. The quarry was last active in 1955 to provide riprap for the Pacific Coast highway near Ventura, Ventura County. Photo taken 1956.

greenstone also may be used for aggregate, ballast, riprap, or fill, if it is available economically.

Some of the most extensive occurrences of greenstone in California are in the Franciscan formation, in the northern and central Coast Ranges, and in the Mississippian (?) Calaveras formation and the Jurassic Amador group along the west flank of the Sierra Nevada. Small amounts of greenstone have been quarried from dike rocks in Los Angeles and San Diego Counties for use as roofing granules; much of the green pyroclastic sedimentary stone quarried in Kern County since World War II for roofing granules could be classed as greenstone. Minor tonnages of greenstone have been produced in the Mother Lode area—including El Dorado, Amador, Calaveras, Tuolumne, and Mariposa Counties—for local use as road rock and fill. In Del Norte County a large tonnage of greenstone was quarried from Preston Island in 1947 for use as riprap in the Crescent City Harbor; pieces as large as 15 tons were used.

*Serpentine.* Serpentine is an ultrabasic igneous rock composed mainly of the mineral serpentine, a hydrous

magnesium silicate. Serpentine rock is moderately soft, but commonly massive and dense in structure, and very resistant to chemical and physical weathering. These properties make it desirable as crushed and broken stone for riprap and fill.

Hundreds of bodies of serpentine occur in the Klamath Mountains, central and southern Coast Ranges, and western flank of the Sierra Nevada, but very little serpentine exists in the southeastern third of the state. Most or all of the serpentine masses in California are alteration products of intrusive peridotites and pyroxenite believed to have been emplaced in late Jurassic or early Cretaceous time.

In the San Francisco Bay area, minor amounts of Franciscan serpentine have been quarried, along with associated sandstone and chert, for use as aggregate, ballast, and fill. At quarries in Oakland, Alameda County; near Clayton, Contra Costa County; near Bayshore, Belmont, and South San Francisco, San Mateo County; and near Los Altos and Madrone, Santa Clara County the serpentine has been obtained largely as a by-product, in the removal of these other rock types.



FIGURE 14. Photo showing Shannahan (Stringfellow Construction Company) quarry in Jurupa Mountains near West Riverside, Riverside County. Cretaceous Woodson Mountain granodiorite has been obtained here intermittently since about 1900, for use as building stone, roofing granules, poultry grit, and, most recently riprap for the Redondo Beach seawall, in 1955, and breakwater in 1956. Photo taken 1956.





FIGURE 15. Photo of Redondo Beach seafront, Los Angeles County, looking southward, showing method of emplacement of granitic riprap stone from Shannahan quarry near Riverside (figure 14). Crawler crane lifts pieces weighing as much as 10 tons from flatbed truck with tong-like pincers, and emplaces them according to directions from engineer standing nearby. Note wreckage of wave-damaged houses just left of crane. Photo taken 1955.

Near Magalia, Butte County, serpentine is quarried for use on roads and driveways. Santa Catalina Island, Los Angeles County, contains one of the few deposits of serpentine in southern California. This deposit yielded dimension stone prior to 1914, and riprap and fill since 1953.

**Shale.** Shale is a very fine-grained, thinly bedded sedimentary rock composed mostly of clay-size and silt-size particles. Shale, commonly containing admixed sand particles, is widely distributed in California and constitutes at least a minor proportion of most of the clastic sedimentary formations present in the state. Pre-Mesozoic shales are commonly well indurated, if not metamorphosed; most Mesozoic and Tertiary shales are moderately to poorly indurated. Shale is particularly abundant in the Jurassic and Cretaceous rocks of the northern and central Coast Ranges and the borders of the Great Valley, and in the Tertiary rocks of the southern Coast Ranges, western Transverse Ranges, and northern Peninsular Ranges.

Most types of shale are too weak to be suited to the ordinary uses of crushed and broken stone. The hard, dense, and siliceous McClure shale of Miocene age has been quarried in at least two localities in Kings County for use as crushed stone. In San Mateo County, a relatively minor tonnage of shale has been quarried, along with sandstone, chert, and conglomerate, from at least four localities in the Jurassic Franciscan and Pliocene Merced formations. This was used on roads and as fill. In Santa Clara County an undetermined tonnage of siliceous shale and chert has been quarried, for highway and fill purposes, from a dozen or more localities in the Miocene Monterey formation. Since 1950 diatomaceous shale of the Miocene Modelo formation has been quarried near Sunland, Los Angeles County, and pulverized for use as insecticide carrier and filler.

**Slate.** Slate is a thinly foliated metamorphic rock composed essentially of muscovite (sericite), quartz, and graphite, all in grains of microscopic or submicroscopic

size. Slate is formed by compaction and partial recrystallization of shale, is commonly dark-colored and moderately hard.

Slate is desired mainly for use as dimension stone (see section on dimension stone). Its chemical inertness, resistance to weathering, and flat particle shape make crushed slate a desirable material for roofing granules and filler dust.

Extensive exposures of slate occur in the Jurassic Mariposa formation, along the western flank of the Sierra Nevada. Minor bodies of slate, mostly of low quality, occur in pre-Tertiary metamorphic rocks at several scattered localities in the state.

Mariposa slate was produced in minor tonnages from a dimension slate quarry dump in Mariposa County in 1926, and from a quarry near Hetch Hetchy Junction, Tuolumne County, from 1931 to 1940. The material from both of these operations was crushed and used mainly as roof granules and filler. The state's principal source of crushed and pulverized slate is the Chili Bar mine, El Dorado County, which has been active since 1926. Here the slate is mined in extensive underground workings and is used for roofing granules and filler dust. Prior to World War II a small amount of Triassic slate of the Bedford Canyon formation was quarried east of Elsinore, Riverside County, and crushed for use as roofing granules. In 1947, slate of undetermined age was quarried north of Keeler, Inyo County, and pulverized for use as filler.

**Tuff.** The term "tuff" embraces pyroclastic, volcanic types, most of which would be classed as rhyolite or dacite tuffs or tuffaceous sediments (see section on pumice, pumicite, perlite and volcanic cinders in this volume). Most tuffaceous rocks are only moderately hard, although on exposure to air they commonly harden appreciably. As many tuffs are attractively colored and workable, they have been extensively used for building stone (see section on dimension stone). Because of its softness, tuffaceous rock is unsuited to most uses of



FIGURE 16. Photo showing limestone-crushing plant of Sno-Top Rock Products Company, near West Riverside, Riverside County, active since 1953. Triassic (?) limestone and marble that contain excessive magnesia are trucked from a nearby cement company quarry. Here this material is crushed, screened, and bagged, mainly for white roofing granules. Fines are used for asphalt tile filler and other industrial purposes. Photo taken 1955.





FIGURE 17. Photo showing roofing granule plant of Sierra Pelona Rock Company near Vasquez Rocks, Los Angeles County. Green granules are made from silicified siltstone of the Oligocene (?) Vasquez formation, obtained from pits in middle distance; red and violet granules from Vasquez volcanic rocks near Vincent; and gold granules from iron-stained granitic rock in Mint Canyon. Pallets of bagged granules in the foreground are ready for shipment. Photo taken 1955.

crushed and broken stone but it is extensively used in the production of colored roofing granules.

Extensive bodies of light-colored tuffaceous rocks occur in the Tertiary volcanic section at many localities in California. Most of the tuffaceous stone that has been quarried in the state has been used for dimension stone. It has been obtained mostly from the Pliocene Sonoma volcanics in Napa, Solano, and Sonoma Counties; from Miocene rhyolite tuffs near Arroyo Grande, San Luis Obispo County; and from Tertiary formations along the west flank of the Sierra Nevada. Small tonnages of waste from these quarries have been used locally for road material and fill. Highly colored Miocene tuffaceous sediments were quarried near Monolith, Jawbone Canyon, and Rosamond, in Kern County, and crushed for use as naturally colored roofing granules at a half dozen crushing plants active in 1955. Roof granules were also produced in 1955 from crushed Pliocene rhyolite-dacite

tuff quarried near Lenwood, San Bernardino County, and from tuffaceous sediments obtained near Vincent, Los Angeles County.

#### USES OF CRUSHED AND BROKEN STONE

Although stone is used in California for many purposes these are divisible into two main classes: (1) "Physical" uses, in which the stone is broken, crushed, pulverized, shaped, or polished, but its physical and chemical characteristics remain essentially unchanged (such as aggregate, dimension stone, filler); (2) "Chemical" uses, in which the stone is changed physically and/or chemically, to yield an end product that differs from the raw stone in composition (such as limestone used in cement and quartz sand used in glass); most uses in this class require stone that is essentially mono-mineralic in composition.

Many various properties of stone may be considered in determining its suitability for a particular type of use. The essential property of stone that determines its selection for a particular use may be primarily physical (such as hardness and durability) or primarily chemical (such as stability in acid or purity of composition). For most uses, however, stone must fulfill both physical and chemical requirements (such as aggregate, which must be physically strong as well as chemically inert).

A few types of stone, notably limestone and vein quartz, are used for physical uses under some circumstances, and for chemical uses under others. Their physical uses, which stem mainly from their physical properties, are discussed below; their chemical uses, which mainly depend on their chemical properties, are described in other sections in this volume (see sections on lime, limestone, and dolomite; cement; quartzite, and quartz).

The category of crushed and broken stone here includes all quarried stone that is not cut or shaped to specified dimensions (see section on dimension stone). It ranges in size from granite blocks weighing many tons used as riprap, to shale ground to smaller than 200 mesh, used as insecticide carrier.

The major uses of crushed and broken stone are described below in alphabetical order.



FIGURE 18. Photo of one of California's largest quarries, the Minnesota Mining and Manufacturing Company operation in Temescal Canyon, near Corona, Riverside County. Jurassic (?) Temescal Wash quartz latite porphyry is blasted down by large-scale coyote-hole blasting methods, crushed, and colored with subvitreous ceramic glazes for use as granules on prepared roofing. Photo taken 1956.



*Aggregate Used in Portland Cement Concrete.* Although several localities in California yield a large tonnage of crushed bedrock specifically for use as portland cement concrete aggregate, most crushed rock that is produced in California for this use, is obtained from alluvial deposits. At most of the larger sand and gravel plants, all cobbles and pebbles too coarse for use as sand and gravel (about  $1\frac{1}{2}$  inches) are screened from the alluvial raw material and crushed for sale as crushed stone for various uses. Sand and gravel are preferred to crushed stone for portland cement concrete aggregate because the natural material is the less expensive and rounded particles give better workability of the wet mix than angular ones. In areas such as the San Francisco Bay area, where a shortage of sand and gravel exists, the high cost of transporting sand and gravel from distant sources overcomes the additional crushing expense of crushed stone. Under these economic conditions crushed stone is commonly used for portland cement concrete aggregate, instead of sand and gravel. Although slightly more care is required in the pouring and placing of a wet mix that contains crushed stone aggregate, the portland cement concrete made with such aggregate is as satisfactory as that made with sand and gravel aggregate of comparable quality.

Because most of the portland cement concrete aggregate produced in California consists of sand and gravel, the reader is referred to the section on sand and gravel in this volume for specifications, costs, and methods of production.

*Aggregate Used with Bituminous Binder.* Asphalt concrete, or bituminous concrete, and bituminous macadam are forms of bituminous-bound aggregate used predominantly for paving (California Div. Highways, 1954, pp. 113-162; ASTM 1954, pp. 27-31).

Table A. Asphalt concrete aggregate. Recommended particle size distribution, proportions of asphalt cement, and possible usage for five typical mixes of asphaltic aggregate. (Asphalt Institute, 1945, p. 4).

Mix no.	I	II	III	IV	V
Use recommended	Lower or intermediate courses*	Inter-mediate or surface courses*	Surface courses*		
Thickness of course*	3-3½"	2½-3½"	2-3"	1½-2½"	1-2"
Sieve size	Combined aggregates, including mineral filler—percent passing by weight				
2½"	100	---	---	---	---
2	95-100	100	---	---	---
1½	80-95	95-100	100	---	---
1	---	---	95-100	100	---
¾	60-75	70-85	---	95-100	100
½	---	---	70-85	75-90	95-100
4	30-45	35-50	40-55	45-60	60-80
10	20-35	25-37	30-42	35-47	40-55
40	12-22	15-25	20-30	23-33	25-35
80	6-16	6-16	12-22	16-24	18-27
200	0-4	2-6	5-10	6-12	8-15
Asphalt cement—pounds per 100 lbs. aggregate	4.0-6.0	4.5-6.5	5.0-7.0	6.0-8.0	6.0-8.5

\* A "course" is a layer of road-building material laid as a unit; most roads consist of a base, leveling, and surface course each with different specifications and functions.

Asphalt (bituminous) concrete consists of a combination of coarse aggregate, fine aggregate, and mineral filler uniformly coated and mixed with asphalt (Asphalt Institute, 1954, pp. 1-2). The types of bituminous-bound concrete that are in general use include road-mixed surfacing; plant-mixed surfacing; asphalt concrete pavement; seal coats; and armor coat (California Div. Highways 1954, pp. 112-162). Each of these types, which are distinguished by particular size gradings of aggregate and different types of bituminous binder, has its own particular usage, and is manufactured in "hot plants," fixed or portable. In these plants aggregate and bitumen are blended and thoroughly mixed at high temperatures to a plastic mass that can be spread in place and finally compacted by heavy rollers. At ordinary temperatures asphalt concrete is hard and unyielding; unlike portland cement concrete, it is slightly plastic under very great or long-applied stresses.

Coarse aggregate for asphalt concrete includes all material retained on the No. 10 sieve. Crushed stone is preferable to gravel in this use because broken surfaces adhere to asphalt better than rounded ones, and the interlocking of angular particles strengthens the concrete. Materials for coarse aggregate must be of reasonably uniform quality, clean, free of excess dust and flat or elongated particles, and have less than 50 percent loss in the Los Angeles rattler abrasion test. Particles must be sound, hard, durable, and free from coatings of clay or other substances. When uncrushed gravel is used, it must have a rough surface texture.

Fine aggregate for asphalt concrete consists of particles that pass the No. 10 sieve but are retained on the No. 200 sieve. It may consist either of sand or finely crushed stone, or a mixture of the two. Grains must be clean, tough, rough surfaced, and free from clay, loam, or other foreign matter.

The mineral filler must pass a No. 200 sieve, and may consist of limestone dust or other approved mineral dust, which is dry and free of lumps and loosely bonded aggregations. In the past, clay and soil in unwashed aggregate have been commonly accepted in asphalt concrete as mineral filler, but most agencies in California now specify that only stone dust be used for mineral filler.

Table A shows recommended particle size distributions, amounts of asphalt cement, and suggested usage for five typical asphaltic concrete mixes. Agencies that use asphaltic concrete may have individual specifications (e.g., California Div. of Highways, 1954, pp. 112-162). A.S.T.M. Tentative Specifications D692-54 (A.S.T.M. 1954, pp. 27-28) gives further details.

Except for mineral filler, aggregate for asphaltic concrete meets the same requirements as aggregate for portland cement concrete, and large commercial plants commonly sell material from the same bins for both uses. Gravel is preferred to crushed stone in portland cement concrete, and crushed stone to gravel in asphaltic concrete, but in localities where only one type of aggregate is readily available it is ordinarily used in both types of concrete.

Bituminous macadam is a type of paving composed of several overlying courses\* of crushed stone laid in pro-

\* A course is a layer of road-building material laid down and compacted as a unit. Two or more courses of different materials and thicknesses are ordinarily superimposed to form a completed road.



gressively finer sizes, each course impregnated with heavy oil and compacted with a roller before the next course is added. Requirements for bituminous macadam aggregate are similar to those for asphalt concrete aggregate, except that little or no mineral filler is used. Macadam was the earliest type of bituminous-bound pavement to be developed, but its service qualities are inferior to asphalt concrete. In recent years "hot plants," for the manufacture of asphalt concrete, have been established in nearly all sections of California, so that little or no macadam pavement is manufactured. Detailed specifications appear in publications of road-building agencies, such as the California Division of Highways (1949, pp. 166-170), and in A.S.T.M. Specifications D693-54 (A.S.T.M. 1954, pp. 29-31). A representative specification for size distribution in bituminous macadam surface appears in table B.

Water-bound macadam pavement, in which fine material or screenings act as the only binder, has similar specifications for quality of aggregate. Disintegrated granitic rock with natural clay binder (see aggregate base) serves most of the purposes of water-bound macadam in California. Requirements for aggregate in water-bound macadam appear in A.S.T.M. Specification D694-54 (A.S.T.M. 1954, pp. 32-34).

Table B. Macadam aggregate. Size grading requirements of aggregate for use in bituminous macadam surface (California Div. Highways 1949, p. 167).

Sieve size	Percentage passing sieve				
	ROCK		SCREENINGS		
	Coarse	Fine	Coarse	Medium	Fine
2½"-----	100	----	----	----	----
2"-----	90-100	100	----	----	----
1½"-----	-----	90-100	----	----	----
1"-----	0-10	-----	----	----	----
¾"-----	0-3	0-10	100	----	----
½"-----	-----	-----	90-100	100	----
⅜"-----	-----	0-3	0-15	90-100	100
No. 4-----	-----	-----	0-4	0-15	90-100
No. 8-----	-----	-----	-----	0-3	0-15
No. 16-----	-----	-----	-----	-----	0-3
No. 200-----	0-1	0-1	0-1	0-1	0-1

**Aggregate Base.** Aggregate base, which includes both untreated base and cement-treated base, is used in highways and paving construction for base courses. Base courses are the lowermost built-up courses that directly overlie the subgrade, or reworked natural underlying material, and support the paving or surface courses (see California Div. Highways 1954, pp. 92-110, and Los Angeles County Road Department Standard Specifications, 1951, Section 38, for descriptions of base courses and types of aggregate base.) Sandy material may be used in the lower base course, or subbase, but crushed stone is preferred for the upper base course, directly beneath the paving courses. The uppermost several inches of the base course are commonly strengthened by the addition of portland cement.

Crushed stone to be used for aggregate base should be free of loam, adobe, vegetable matter, and other detrimental substances. It must compact and bind readily under rolling, have low plasticity, low expansion, and high bearing ratio.



FIGURE 19. Photo of California's largest active slate mine, the Pacific Minerals Company, Ltd., operation at Chili Bar, north of Placerville, El Dorado County; view southward across the American River. Steeply dipping Jurassic Mariposa slate was obtained in the early 1900's from the quarry face shown for roofing slate; since 1928 it has been quarried in huge underground chambers and crushed to produce roofing granules for prepared roofing and filler dust. Photo by Mort D. Turner.

Throughout most of California the crushed stone that is used for aggregate base is of the same quality as that used for concrete aggregate but limits of size distribution are broader, and a higher percentage of fines is permissible in aggregate base than in aggregate.

In southern California, thoroughly weathered granitic rock known as decomposed granite or "DG" is commonly used as aggregate base. Ideally decomposed granite deposits contain stone weak enough to be quarried without explosives and to require little crushing or screening, and yet strong enough for compaction into a stable base course. Clay content should be low enough to avoid plastic flow and permit good drainage. California Division of Highways specifies 3 to 9 percent passing No. 200 sieve, and also requires plasticity tests.

Hundreds of sources of decomposed granite have been worked in the Los Angeles area for use on local paving projects, mostly on contract for municipal agencies.

Most aggregate base is used for roads, parking lots, and other paved surfaces, but small amounts are used for temporary surfacing with only the clay naturally present to act as binder. Except for crude crushing and screening at some deposits, decomposed granite is not processed for use. It is one of the least costly grades of crushed stone and commonly is sold for about 50 cents a ton f.o.b. pit.

**Fill.** Most fill material is natural earth obtained as surplus from excavation or from borrow pits, and would not be classed as stone. Structure backfill, as defined by





FIGURE 20. Photo showing sacking of marble terrazzo granules at plant of Sonora Marble Aggregate Company near Sonora, Tuolumne County. Operator fills sack with 100 pounds of granules from automatic measuring hopper; sacks are conveyed on belt to sewing machine (left), where top is sewn shut; sacks are then stacked on pallet (right) for loading by fork-lift truck. Photo by Mary Hill, 1956.

California Div. Highways, 1954, p. 66, contains no stones or lumps larger than four inches in greatest dimension, and has sand equivalent value of not less than 30 (see section on sand and gravel in this volume). Crushed stone is used for special types of fill, such as the cores of dikes or dams. Only the least expensive grades of crushed stone, commonly crusher-run fines or unclassified waste from production of riprap, are used for fill. Decomposed granite is occasionally used for fill where a project requires strong and low-shrinking material, such as sub-basement fill under buildings.

**Poultry Grit.** A minor but active segment of California's crushed stone industry is the poultry grit industry. All birds need sharp, hard, gritty rock fragments in their gizzards to enable them to "chew." Domestic poultry commonly lack access to natural rock fragments and must be constantly supplied if they are to thrive. Rock for poultry grit should be as hard, as sharp, and as insoluble as possible, and be free from organic or other impurities. It should maintain a sharp cutting surface throughout its period of use, and wear by flaking of the particle surface rather than by dissolution. Poultry grit is commonly made from crushed granitic rock; occasionally from anorthosite and vein quartz. Poultry grit is distinct in nature and purpose from the crushed limestone given poultry as a food supplement to provide lime (see section on lime and limestone), although both are commonly mixed with the poultry feed.

Several thousand tons of poultry grit, ranging in size from number 26 to number 4 sieve, are consumed each year in California, by domestic birds ranging in size from parakeets to turkeys. An undetermined tonnage is provided from crushed alluvial material, by sand, gravel, and crushed stone producers, and from standard sizes of crushed stone aggregate. The largest producer of poultry grit in California is the Haven Granite Company who since 1952 have obtained Cretaceous (?) granitic rock

from the Guy F. Atkinson quarry in West Riverside, Riverside County, and crushed it solely for use as poultry grit. Material from this plant is marketed in six standard sizes throughout the western states and Hawaii.

Most poultry grit is marketed in 100-pound bags, for prices in the range of \$15 to \$20 per ton, f.o.b. mills, depending on sizing and tonnage.

**Railroad Ballast.** Railroad ballast (see Goldbeck, A.S.T.M. 1948, pp. 197-204; Smith, 1956) is the rock material placed on the roadbed, and on which the ties are laid (figure 2). It mainly acts as a non-rigid foundation support to stabilize the ties against the stresses of traffic and the expansion in the rails due to temperature changes. Ballast also aids drainage of water from the ties, helps in maintaining a uniform grade and alignment of the track, and retards the growth of vegetation.

Crushed stone is widely used as ballast. Moderate tonnage of crushed slag from abandoned smelters are used for ballast in northern and central California: crushed blast furnace slag is used extensively for ballast in other states. About 14 percent of the ballast used in California is sand and gravel that contains some crushed particles. In 1952 California yielded 526,654 short tons of crushed stone valued at \$404,843 for railroad ballast, an average of \$0.77 per ton, compared to the national average of \$0.94 per ton. Nearly two-thirds of California's production of ballast consists of crushed cobbles and boulders obtained from alluvial deposits. The remainder is divided among granitic rocks, volcanic rocks, and sandstone.

Material for use as ballast should be hard and tough enough to resist shattering by tamping tools, and wear from vibration of the ties under rail traffic. Soundness, or resistance to freezing and thawing, is required to prevent disintegration from weathering. American Railway Engineering Association specifications (A.R.E.A. Bulletin 437, 1943, p. 532) state maximum allowances of 5 percent soft and friable pieces; 1 percent material finer than No. 200 sieve; and 0.5 percent clay lumps. Forty percent loss in the Los Angeles Rattler abrasion test is generally the maximum acceptable limit; 10 percent is the maximum acceptable loss in 5 cycles of the sodium sulfate soundness test (see discussion of testing in section on sand and gravel in this volume). These requirements are about the same as those for crushed stone used as portland cement concrete aggregate. The importance of particle shape is incompletely understood (Smith 1956). Sand and gravel may be suitable for ballast if a certain proportion, commonly ranging from 20 to 70 percent, of angular fragments are present.

Nominal sizes for five main classes of ballast are  $2\frac{1}{2}$  to  $\frac{3}{4}$  inch; 2 to 1 inch;  $1\frac{1}{2}$  to  $\frac{3}{4}$  inch; 1 to  $\frac{3}{8}$  inch; and 1 inch to No. 4 mesh. A recent trend has been toward the use of smaller sizes of ballast. The blending of particle sizes in correct proportions (figure 3) is critical, especially for ballast that contains a substantial proportion of rounded fragments (Smith 1956).

Ballast is prepared by crushing and screening suitable stone to the desired size range. Plants that process commercial sand, gravel, and crushed stone in the Los Angeles and San Francisco areas sell crushed alluvial cobbles and boulders as ballast. The standard commercial grade of crushed stone which is known as  $1\frac{1}{2}$ -inch and is graded between 2-inch and  $\frac{3}{8}$ -inch screen sizes is



Table C. Relation of density (pounds per cubic foot) to weight (short tons) of riprap in several size classes for use in Moss Landing Harbor (from U.S. Army Corps of Engineers specifications). When stone of given density is used, pieces must be of indicated tonnage to result in stable riprap structures.

		Density (pounds per cubic foot)			
		145-154	155-164	165-174	175+
C L	50% of total weight in pieces not lighter than:	(tons) 14	(tons) 10	(tons) 8	(tons) 6
A S S 1	Remaining 50% graded in the interval:	7-14	5-10	4-8	3-6
C L	50% of total weight in pieces not lighter than:	7	5	4	3
A S S 2	Remaining 50% graded in the interval:	3-7	2-5	2-4	1½-3
C L	50% of total weight in pieces not lighter than:	3	2	2	2
A S S 3	Remaining 50% graded in the interval:	1-3	1-2	1-2	1-2

widely used for ballast in southern California. Large tonnages of cobbles from gold dredger tailings near Oroville, Butte County, are crushed to provide ballast for use in northern California. Andesitic rock quarried near Newberry, alluvial fan material obtained at Afton Canyon, and volcanic cinders from Mt. Pisgah, all in San Bernardino County, as well as volcanic cinders obtained near Little Lake, Inyo County, provide ballast in southeastern California; granitic rock is crushed for ballast at Piedra, Fresno County. Many alluvial deposits and stone quarries have yielded ballast in outlying districts of the state. Much of the ballast used by the major railroads is produced by the companies from their own quarries.

Ballast is a low-cost crushed stone product that is ordinarily obtained as close as possible to the site of use in order to reduce transportation expense. Costs of railroad produced ballast are not available for publication. Commercial crushed stone costs about the same as for aggregate; \$1.20 per ton is obtained by one large producer for 1½-inch crushed stone, f.o.b. plant, in the Los Angeles area.

**Riprap.** Riprap, the heavy irregular fragments of broken stone, or other resistant substances, which are placed without mortar to provide protection from the physical erosive action of water, consists of blocks that range in weight from 35 tons to less than 100 pounds. For some projects, pieces weighing as little as 2 pounds are specified (table D). It is extensively used in river and harbor areas to protect against waves, tides, strong currents, and flood waters. Smaller tonnages are used to protect railroad embankments, dam spillways, and bridge abutments.

The principal requirements of stone to be used as riprap are (1) durability to resist the physical and chemical attack of water; and (2) a specific gravity



FIGURE 21. Photo showing poultry grit plant of Haven Granite Company, West Riverside, Riverside County. Cretaceous (?) granitic rock from the nearby Gay F. Atkinson Company quarry is crushed to variously sized granules to enable domestic fowl to masticate. Photo taken 1936.

high enough to prevent pieces from being moved by water action. Riprap specifications ordinarily require stone to be sound, durable, free from laminations or weak cleavages, and of such character that it will not disintegrate from the action of water. The specific gravity should be at least 2.5. Loss in the Los Angeles Rattler abrasion test (see sand and gravel section for description of test) should not exceed 40 percent for 500 revolutions (California Div. Highways, 1954, p. 269). As long as these physical requirements are fulfilled any type of rock may be used; chemical and mineral composition of the rock is of minor importance. The riprap structures that have been emplaced in California have been more damaged by the dislodging of stones from the structure by wave action than by disintegration or breaking of individual pieces. Density of the stone is an important factor in determining the stability of the structure. The minimum size of stone required for stable riprap varies approximately with the cube of the density.

Table C, taken from U. S. Army Corps of Engineers specifications for Moss Landing Harbor, Monterey County, illustrates the relation of density of stone to size required.

Riprap should be emplaced, with reasonable regard to the size and shape of pieces, so as to (1) leave a minimum of voids, (2) result in a minimum of breakage, (3) stagger horizontal and vertical joints, (4) place the long axis of the stone normal to the long axis of the structure, (5) to tilt the long axis of the stone down slightly toward the center of the structure (U. S. Army Corps of Engineers, Specifications for Crescent City Harbor project).

Size classifications of riprap differ for different projects and different specifying agencies. The designations "A-stone," "B-stone," "C-stone," and "D-stone" are applied to various size ranges of stone in order of decreasing size. A-stone, sometimes called capstone, derriek stone, or armorstone, is the largest size and ordinarily is used as a facing to protect the smaller sizes that make up the core of the structure. Overlap of sizes in adjacent size ranges is common.

As transportation costs figure heavily in the ultimate cost of delivered riprap, it is obtained as near the site of use as suitable rock can be found. In different parts of California different types of stone are used, depending on their availability. The main use of riprap in northern California is for jetties and breakwaters in harbor development projects supervised by the U. S. Army Corps



Table D. Examples of riprap grading

A-Stone	B-Stone	C-Stone	D-Stone
1. At least 50% of total tonnage of this class in pieces heavier than 10 tons; none lighter than 1 ton.	At least 35% of total tonnage of this class in pieces heavier than 2 tons; at most 20% in pieces lighter than 20 pounds; at most 5% in pieces lighter than 1 pound.	"Earth core"—no size specification.	
2. 100% of total tonnage of this class in pieces weighing between 1 and 6 tons; at least 50% heavier than 3 tons.	40% of total tonnage of this class in pieces weighing between 1 and 5 tons; at most 25% lighter than 100 pounds; at most 5% lighter than 1 pound.	Total tonnage in this class in pieces lighter than 1000 pounds; at most 10% heavier than 100 pounds; about 25% between 10 and 100 pounds; at least 50% heavier than 10 pounds; at most 5% of any one load earth and fines.	
3. ("Derrick stone") Total tonnage in this class in pieces weighing between 5 and 4500 pounds; 20% between 1500 and 4500 pounds; 60% between 450 and 1500 pounds; 15% between 100 and 450 pounds; 5% between 5 and 100 pounds.	("Riprap") Total tonnage in this class in pieces weighing between 2 and 500 pounds; 20% between 185 and 500 pounds; 60% between 7 and 185 pounds; 20% between 2 and 7 pounds.	("Spalls") Total tonnage in this class in pieces between No. 4 screen and 9 inches in size.	("Filler material") Total tonnage in this class in pieces between No. 100 screen and 1½ inches in size.
4. Most material in the weight range from 1 to 10 tons; pieces as large as 35 tons when required.	("Riprap") Total tonnage in this class larger than 12 inches diameter and weighing less than 2 tons.	Total tonnage in this class in pieces between 6 and 12 inches in diameter.	("Crusher-run base") Total tonnage in this class in pieces smaller than 2 inches in diameter, including all fines produced during crushing.
5. ("Armor stone"). Total tonnage in this class in pieces weighing between 7 and 17 tons, but averaging not less than 12 tons.	Total tonnage in this class in pieces weighing between 2 and 7 tons, at least 50% heavier than 4½ tons.	Total tonnage in this class in pieces ranging from 2 tons weight to rock dust; at least 40% heavier than 500 pounds; at least 60% heavier than 200 pounds; at most 10% lighter than 5 pounds.	

## SIZE GRADE SPECIFICATIONS FOR RIPRAP OBTAINED FROM FOLLOWING SOURCES:

1. U. S. District Engineer's specifications for detached breakwater, Los Angeles Harbor.
2. Los Angeles City Engineer's specifications for jetty at entrance to Fish Harbor.
3. U. S. Army Corps of Engineers specifications for flood control channel linings in Los Angeles harbor areas.

4. Size of stone commonly produced at Santa Catalina Island quarries (Gay and Hoffman, 1954, p. 331).
5. U. S. Army Corps of Engineers specifications for breakwater stone, Crescent City Harbor project.

of Engineers. Tough arkosic sandstone of the Franciscan formation or similar to it, has been quarried in several nearby localities for use in the harbors at Crescent City, Del Norte County; Humboldt Bay and Noyo, Humboldt County; and Bodega Bay, Marin County. Quarries in Franciscan sandstone at McNear Point in Marin County, and Point Richmond in Contra Costa County, have yielded most of the riprap for projects in the San Francisco Bay area. Granitic rock of the Santa Lucia formation quarried at Logan, San Benito County, and in Monterey, Monterey County, has been used at Moss Landing and Monterey harbors. In addition, metamorphosed Franciscan sandstone from Brisbane, San Mateo County, was used at Moss Landing and granitic rock from Rocklin, Placer County, was used at Monterey.

A shortage of suitable stone for riprap exists in the vicinity of the Los Angeles harbor at San Pedro. Abundant granitic and metamorphic rocks exist in the San Gabriel Mountains but are generally too fractured and decomposed to be suitable. Cretaceous sandstone quarried near Chatsworth, Los Angeles County, was used in the San Pedro breakwater built about 1906 (Anbury 1906, p. 130). Since then nearly all riprap used in the Los Angeles areas has been obtained from occurrences of relatively unweathered Cretaceous (?) granitic rocks near Riverside in San Bernardino and Riverside Counties, or from Mesozoic (?) metaconglomerate, serpentine, and metavolcanic rocks barged from Santa Catalina Island (Bailey 1954, geologic map). The cost of barge haulage from Santa Catalina Island to coastal points in Los Angeles County is considerably less than that of truck or rail haulage from most of the inland sources of

riprap. Riprap for San Diego harbor projects is obtained mainly from quarries in Peninsular Range granitic rocks near Santee and Escondido, San Diego County. The relatively minor tonnages of riprap placed along highway and railroad embankments throughout the state are obtained from various localities which are mostly near the point of use.

Portland cement concrete blocks, either scrap or made to order, and concrete-filled sacks are sometimes used for riprap when satisfactory natural stone is unavailable. At Humboldt Bay concrete cubes that weighed as much as 100 tons and tetrahedrons that weighed 4 to 8 tons each were emplaced as riprap along the sides and ends of jetties.

Riprap is produced by relatively simple open-pit quarry methods, almost entirely from side-hill quarries where exposures are good and waste disposal simple. The rock is broken by explosives which are detonated in churn or pneumatic drill holes or in coyote holes. Large cranes are used to sort and load required sizes of stone on trucks, railroad cars, or barges for haul to the site of use. Smaller sizes of riprap may be dumped in place, but the larger stone is carefully emplaced by cranes (figure 15).

Riprap is among the lowest cost varieties of broken stone, because it is used essentially in the form that it is quarried, and requires little handling or classification to size. The large tonnages ordinarily used in a given project enable the application of large-scale, low-cost production methods. Many of the quarries that yield riprap, although large, are intermittently active or are worked only during the life of a project. Riprap is com-



monly sold for about \$5 to \$10 per ton emplaced. As much as half of the price may be transportation cost. Large riprap quarried in 1955 from granitic rock near Riverside, for use on the much-publicized Redondo Beach sea wall, cost about \$8 per ton in place; trucking costs were about \$3.50 per ton for the 70-mile haul, according to project engineers. In 1953, the U. S. Army Corps of Engineers spent about \$100,000 to establish a quarry in Franciscan sandstone at Pt. St. George, Del Norte County, to obtain stone for the Crescent City Harbor project, about 5 miles away.

After this initial outlay, \$6 per ton was paid for 41,000 tons of A-stone, \$4.50 per ton for 23,000 tons of B-stone, and \$4 for 29,000 tons of C-stone, all emplaced. Prices between \$2 and \$2.25 per ton were quoted for granitic riprap stone for the Moss Landing project, f.o.b. quarries, in 1952. The accepted bid on that project was \$7.50 per ton for A-stone, and \$6.00 per ton for B- and C-stone, emplaced, according to the U. S. Army Corps of Engineers.

**Roofing Granules.** Crushed stone granules are used widely in California as a covering for asphalt-base roofs. Two main types of asphalt roofing—built-up and prepared—are in general use. Prepared roofing consists of asphalt-impregnated felt which is covered with fine rock particles during manufacture. It is sold in shingles or rolls ready to nail in place. Built-up roofing, on the other hand, is assembled on the job, and consists of successive courses of asphalt-impregnated felt laid on the roof, with hot roofing asphalt applied on top of each course. Rock granules are spread over the uppermost coating of tar, which solidifies and holds them in place. The purpose of the roofing granules is the same in each type of roof: to protect the asphalt from actinic rays of the sun, to prevent deterioration, cracking, and water penetration.

Materials for roofing granules can be classified as (1) natural rock, including white, black and colored types; (2) artificially colored rock; and (3) artificial substances. White natural rock granules are mainly limestone or dolomite; black natural rock granules are mainly slate or alluvial grains of dark minerals such as ilmenite. Colored natural rock granules are mainly tuffaceous volcanic rocks in various shades of red, pink, brown, and green, but also include red or gold-colored granitic rocks, dark red volcanic cinders, and green metamorphic rocks. Artificially colored granules are made by coating closely sized fragments of suitable volcanic rock with subvitreous ceramic glazes of the color desired.

Nearly all of the artificially colored granules produced in California are made at Corona, Riverside County, from Jurassic (?) Temescal Wash quartz latite porphyry.

The artificial substances that are crushed for roofing granules are mainly rejected or used ceramic products such as sewer tile, common brick, fire brick, glazed wall tile, and sanitary whiteware. Crushed blast furnace slag and expanded shale also are employed.

Granules for built-up roofs should be (1) opaque to actinic rays, (2) clean (minimum of dirt or fines), (3) dry, and (4) hard. Opacity protects the asphalt. Cleanliness permits the granules to stick well, as dust would coat the hot tar surface and prevent a clean contact with the larger granules as they are emplaced. Less than 3

percent, by weight, of granules should be fines. Hardness keeps dust from forming, by attrition between granules, while the sacks are transported to the job. Dryness (lack of free moisture) also enables the granules to stick well.

In addition to these basic requirements, the color, particle shape, size grading, and surface texture of the granules are commonly considered to be important qualities. Colors should be pleasing to the eye, resistant to fading or staining, and reasonably uniform for a given type of granule. White granules, very popular in California in the 1940's, were superseded in popularity by colored granules in the early 1950's. Subdued, pastel shades of green, blue, red, pink, and brown are popular among the colored granules. Several colors occasionally are blended to produce special effects. On large flat roofs of tall industrial or public buildings, where appearance is of minor importance, gray granules, made of blast furnace slag or alluvial pea gravel, are commonly used.

Particle shape is the principal factor in determining the degree of coverage, and also markedly influences the adhering qualities. Flat, wedge-shaped particles give optimum coverage per ton of granules; angular particles make a better bond with the asphalt than rounded ones.

Normal size gradings for standard granules are ordinarily in the range of about  $\frac{3}{4}$  to  $\frac{1}{2}$  inch. Granules graded evenly throughout their nominal size range give optimum coverage, as the finer particles fill the open spaces between the larger ones. Finer size gradings give more extensive coverage per ton of granules, but the thinner the granule layer, the less it protects the roof. An increasingly popular practice is to place rock particles as large as 3 inches in maximum dimension on top of the standard size granules for the textural effect; such oversize granules are termed "shadow rock."

The nature of the surface of the granules may affect the bond with the asphalt as porous granules may cause deterioration of the asphalt by drawing the light oil fractions out of the asphalt by capillary action. Such granules may themselves be discolored by the dark oils.

Rock for built-up roof granules is obtained and milled as close to main areas of consumption as possible. Southern California is the center of production and consumption in the state. Naturally colored granules are milled in Kern County, near Rosamond, Tehachapi, and Mojave; in San Bernardino County, near Barstow; in Los Angeles County, near Acton and Azusa; and in San Diego County, near Jacumba. White granules are mainly obtained near Victorville and Adelanto, San Bernardino County; near Riverside and Palm Springs, Riverside County; at Columbia, Tuolumne County; at Shingle Springs, El Dorado County; and near Santa Cruz, Santa Cruz County. Many firms which crush limestone or dolomite for other purposes sell small amounts for roofing granules. The Kaiser Aluminum and Chemical Corporation dolomite quarry at Natividad, Monterey County, yields a large tonnage of roof granules that are transported as far as the Los Angeles area. Wall-tile, sewer-tile, and similar industrial waste are crushed at mills in the Los Angeles area to make granules for built-up roofs. A small percentage of artificially colored granules made at Corona, Riverside County, and Puente, Los Angeles County, are used for built-up roofs, as are minor amounts of the volcanic cinders quarried near Little Lake, Inyo County. The production of colored granules



in central and northern California is relatively minor and large tonnages are shipped into these areas from sources in southern California. Dark gray to black granules are produced from slate at Chili Bar, El Dorado County; aluminum was formerly used on these granules to increase reflectivity. Greenstone, obtained in underground workings at Angels Camp, Calaveras County, also has been used to make green granules.

Production methods are similar throughout the industry. Rock of desirable color and quality is sought in quarry sites as close as possible to the mill and to markets. After it has been drilled and blasted, rock is loaded by front-end loaders to trucks which haul it to the mill. After passing a grizzly, usually with 5- to 8-inch openings, the rock is crushed to about minus two inches in a jaw crusher. It is then screened on vibrating screens, the standard  $\frac{1}{8}$  to  $\frac{3}{4}$  inch size going to a bin for sacking in 90- or 100-pound paper sacks, tied with a wire. The fines are discarded, while oversize particles are re-crushed in a secondary crusher, ordinarily a roll crusher, and returned to the screen. If shadow rock is desired, a different screen may be used or oversize particles from the standard screen may be sacked directly. Special dust-collecting apparatus is used at some mills.

Nearly all granules are sold sacked f.o.b. mill, to dealers in roofing materials. In 1956 white granules were marketed for about \$8 to \$11 per ton and natural colored granules for about \$13.50 to \$16.50 per ton. The relatively minor tonnage of granules shipped in bulk by truck or rail cost one or two dollars a ton less. Transportation and handling costs add about \$5 to \$10 per ton for granules at distributors' warehouses.

Built-up roofs are used in temperate, snow-free parts of the state where flat or gently sloping roofs are practicable. Large tracts and new housing developments near the main population centers provide the market for most of the state's output of roofing granules. Minor tonnages are used in smaller cities and some are shipped out of state to destinations as distant as Denver, Colorado.

The artificially colored granules which are used on prepared roll and shingle roofing are mostly in the range 10 to 35 mesh. Physical specifications as to opacity, cleanliness, dryness, hardness, and uniformity of color are similar to those for the granules used on built-up roofs.

The principal manufacturer of artificially colored granules in California is the Minnesota Mining and Manufacturing Company, whose quarry, plant and offices are at Corona, Riverside County (Utley, 1949). This company operates one of the state's largest quarries in a body of Jurassic (?) quartz latite porphyry. In a plant at the quarry this rock is crushed, screened and coated with a subvitreous ceramic glaze. A wide selection of colors is produced; some of the most popular are pastel shades of red, green, and blue. Granules are distributed to prepared roofing manufacturers in the Los Angeles and San Francisco areas, and various out-of-state localities, some as distant as Vancouver, British Columbia.

**Terrazzo.** Terrazzo is a type of floor surface that consists of marble granules embedded in portland cement and sand matrix, with the surface machined and polished to a high gloss finish. Most terrazzo is laid and surfaced in place, but in recent years an increasing number of plant-cast slabs of terrazzo have been used for steps, building facings, and various decorative applications.

Terrazzo surfacing is commonly about five-eighths of an inch thick, but it may range from a quarter of an inch to one inch in thickness. The mixture consists of about 70 percent marble granules, and about 30 percent portland cement; one or two percent of aluminum oxide grain abrasive may be added to improve traction. Decorative effects are achieved by the use of granules of different sizes and color combinations, and by using various colored cements.

For use as terrazzo granules, marble fragments should be hard, dense, free from soft or friable material, dirt, shale, mica, organic matter, loam, and other deleterious substances. Colors and size proportions are optional; the following sizes were specified for one large project (Metropolitan Water District specifications 731, La Verne Filtration Plant, Los Angeles County, p. 84):

No.	Mesh (inches)	Percent
1-----	$\frac{1}{8}$ — $\frac{3}{8}$	20
2-----	$\frac{3}{8}$ — $\frac{5}{8}$	30
3-----	$\frac{5}{8}$ —1	50

(with not more than 10 percent marble dust).

Commonly used commercial sizes of terrazzo granules are No. 1:  $\frac{1}{8}$  to  $\frac{1}{4}$  inch; No. 2:  $\frac{3}{8}$  to  $\frac{5}{8}$  inch; and No. 3:  $\frac{1}{2}$  to  $\frac{5}{8}$  inch. An 8-mesh granule and a mixture of sizes known as "Venetian mix" are also produced in California.

An estimated 5 to 10 thousand tons of terrazzo granules are consumed in California each year, chiefly in the southern California area. The sources of this material include a number of other states and foreign countries; less than 1,000 tons of terrazzo granules are produced each year in California.

Although minor amounts of terrazzo granules have been quarried in the past in Inyo, Tuolumne, and Santa Cruz Counties, since 1950 only one firm with quarries near Sonora, Tuolumne County, is known to have been an active supplier of terrazzo granules. In this operation, marble of the Mississippian Calaveras formation is crushed to form granules; colors produced are white, yellow, ivory, gray, blue, green, black, and red. This output is marketed almost entirely in California, for prices ranging from \$21.50 to \$43 per ton, according to size and color, f.o.b. truck at Sonora, minimum lots 20 tons. Retail prices in California depend on color, size, quantity, quality, and source, and range from \$2 to \$4 per 100-pound sack, delivered.

Early in 1956 the first known pre-stressed terrazzo slabs were manufactured in the Los Angeles area. These are poured  $\frac{5}{8}$ -inch thick in 3- by 500-foot beds, along which 16-gauge wires are stretched at one-inch intervals, to 150,000 psi tension. When the cement hardens the slab is surfaced and sawed into usable sizes with each dimension a multiple of 18 inches. These slabs were being retailed for about \$1 per square foot.

Granules other than marble are used in a minor proportion of the prepared stone surfacing made in California. Because most other usable types of granule are much harder than marble, the costs of sawing, grinding, and polishing are higher than for terrazzo. Two manufacturers, one in the San Francisco area and one in the Los Angeles area, each make two types of prepared stone surfacing, known as "mo-sai stone" and "reconstructed granite." Each is a terrazzo-like surface, in which granules of quartz and granitic rocks are embedded, either



Table E. Minor uses of crushed and broken stone.

Field of use	Type of rock	Function	Remarks
Abrasives.....	Quartzite, nepheline syenite, granite. Clay, diatomite, limestone, pumice, tripoli, soapstone. Quartz, garnet, emery, quartz, quartzite. Granite.	Pebbles in grinding mills. Polishing, lapping, and buffing powder; dentrifice; cleansing compounds. Sandpaper, sandblasting, emery paper ingredient, in carborundum. Poultry grit; to enable fowl to masticate.	See sections on abrasives; cement; clay; diatomite; lime, limestone, and dolomite; pumice, pumicite, perlite and volcanic cinders; quartzite and vein quartz; specialty sands; talc and soapstone.
Agriculture.....	Diatomite, perlite and pumice, volcanic cinders. Limestone, marl, gypsum, sulfur-bearing volcanic rock, granitic rock. Quartz, tuffs. Granitic rocks. Shale, diatomite, pyrophyllite. Limestone (seashells and calcite).	Improves physical condition of soil.  Improves physical and chemical condition of soil; adds nutritive values. Chinchilla dust baths. Poultry grit. Insecticide carrier, fluffing agent. Supplemental source of calcium carbonate for poultry, cattle feed.	See sections on diatomite; gypsum and gypsum; lime, limestone, and dolomite; pumice, pumicite, perlite and volcanic cinders; phosphates; and sulfur; also see Jenny, and others, 1951.
Ceramic industry.....	Quartz, quartzite, limestone.  Quartzite, limestone. Quartzite.	Ingredient in body of various whitewares and frits. Body and binder of silica refractory bricks. Placing or potters sand.	See sections on lime, limestone, and dolomite; specialty sands; vein quartz and quartzite.
Chemical industry.....	Limestone. Quartz, quartzite.	Acid neutralizer, etc. Catalyst carrier in oil refinery processes.	See sections on lime, limestone, and dolomite; quartzite and quartz.
Cigarette urns.....	Limestone.	Clean, attractive appearance.	See section on specialty sands.
Filler.....	Clay, diatomite, limestone, soapstone, quartz, talc, pyrophyllite.	Inert, colorless extender; various specific functions depending on field of use.	See sections on clay; diatomite; lime, limestone, and dolomite; pyrophyllite; talc and soapstone; quartzite and quartz.
Filters..... (Sewage trickling)	Granitic types (unspecified)	Form porous bed to carry aerobic bacteria.	See section on specialty sands.
Glass, mineral wool, soluble silicates.....	Quartzite.  Limestone.	Ingredient to provide silica (SiO <sub>2</sub> ).  Ingredient to provide lime (CaO).	See sections on specialty sands; iron industries—slag; lime, limestone, and dolomite.
Metallurgical industries.....	Limestone. Quartz, quartzite, quartzite "ganister."	Fluxstone. Placing or potter's sand. Cupola and ladle linings.	See sections on iron industries; lime, limestone, and dolomite; specialty sands.
Rock dusting.....	Limestone.	White-colored inert dust to prevent coal mine dust explosions.	See section on lime, limestone, and dolomite.
Whiting.....	Limestone.	Inert, white colored (like filler).	See section on lime, limestone, and dolomite.

alone or in combination. Mo-sai stone is surfaced by removal of part of the cement by etching and abrasion, exposing portions of the granules in bas-relief. Reconstructed granite is surfaced by grinding and polishing methods, which result in a finish similar to polished granite.

Granules for these materials must be hard, sound, durable, non-absorptive, and otherwise meet the specifications for high quality portland cement concrete aggregate. Furthermore, they must have suitable color and texture for the desired appearance. They are crushed, graded in nominal sizes ranging from 1½ inches to about ⅜ inch, and delivered to prepared stone manufacturers in 100-pound sacks, for prices ranging from \$30 to \$60 per ton.

Approximately 1,000 tons of these granules are consumed a year in California, all supplied by established stone producers from local quarries operated principally for other purposes.

Another terrazzo-like specialized use of crushed stone is in the manufacture of streetlamp poles. The poles are made in molds in which wires have been pre-stressed longitudinally to 120,000 psi. The mold is partly filled with specially prepared concrete and spun on its long axis so that centrifugal force presses the concrete against

the mold and leaves a hollow conduit for electric connections down the center.

Different colors and types of aggregate and cement have been used to achieve various appearances in concrete light poles in the past. In recent years a combination of white marble and dark granitic rock granules, with gray cement, have been most popular. When almost dry the pole surface is abraded and etched to remove almost all the exposed cement and leave an exposed aggregate texture in a pepper-and-salt color.

Granitic rock granules have been obtained in Riverside County, and marble granules from Tuolumne County for this use; specifications are essentially as listed above for other types of prepared stone surfacing. Because only one firm, located in the Los Angeles area, manufactures concrete lamp poles in the western states area, details as to price and tonnages of aggregate consumed in this industry are not available for publication.

**Other Uses.** Relatively small tonnages of crushed and broken stone of many types are used by a wide variety of industries for a broad range of purposes. Many of these require rock of a particular type, such as limestone or quartz, and are further described in sections on these commodities. Some of the minor fields of use of crushed and broken stone are summarized in Table E.



Table F. Principal sources of crushed and broken stone in California, by stone-producing districts.

## NORTH COAST AREA

Del Norte County	(O'Brien 1952, pp. 279-280, 308).
basalt	Dark volcanic rock, of undetermined age, quarried at Pt. St. George in 1949 for riprap for Crescent City breakwater.
sandstone	Franciscan (?) sandstone quarried at Pt. St. George in 1949 for Crescent City breakwater riprap.
greenstone	Dense greenstone of undetermined age, quarried at Preston Island in 1947 for Crescent City breakwater riprap.
undetermined	Undetermined stone quarried at Rowdy Creek since 1953 for unspecified crushed stone usage.
Humboldt County	(Averill 1941, pp. 527-528).
basalt	Tertiary (?) anorthoclase trachyte quarried near Arcata; and massive meta-andesite, age undetermined, quarried near Trinidad in 1940's for riprap in Humboldt Bay jetty; prior 1941 at Trinidad for aggregate.
sandstone	Franciscan (?) sandstone quarried in late 1940's near Humboldt Bay for riprap use there.
Mendocino County	(O'Brien 1953, pp. 367-370).
sandstone	Franciscan (?) sandstone quarried in late 1940's near Noyo for riprap in Noyo harbor.
Siskiyou County	(O'Brien 1947, pp. 454-455, 460).
carbonate rock	Paleozoic limestone quarried in minor tonages near Gazelle; prior to 1930 for lime manufacture, in 1945 for sugar rock, and in 1947 for "carbide rock". Minor amounts of quarry waste used locally for crushed stone.
sandstone	Lower Cretaceous Chico sandstone quarried in at least three localities near Yreka and Hornbrook in the early 1900's for railroad culverts and building stone.
Trinity County	
undetermined	Undetermined type of rock quarried in 1952-1953 near Island Mountain for railroad ballast and riprap.

## SAN FRANCISCO BAY AREA

Alameda County	(Davis 1950, pp. 318-337; 340-341).
sandstone	Franciscan sandstone, partly metamorphosed, quarried at several large pits along the west side of the Berkeley Hills, from Berkeley to Niles; used for aggregate, railroad ballast, fill, macadam, road rock, roofing granules, riprap; all pits inactive since prior to 1950, mainly because of encroaching housing developments.
serpentine	Franciscan (?) serpentine quarried near San Leandro for aggregate, etc.
chert	Franciscan (?) chert ("red rock") quarried from large pit in western San Leandro Hills; used for aggregate, fill, etc., since 1931.
chert-conglomerate	Franciscan (?) metamorphosed chert and conglomerate ("red rock") quarried since 1946 near Niles for aggregate, etc.
undetermined	Undetermined types of rock quarried in 1952-1953 at Newark and Oakland; and prior to 1950 near Hayward and San Leandro for macadam, aggregate, fill, ballast and riprap.
Contra Costa County	(Laizure 1927, pp. 21-29; Davis and Vernon 1951, pp. 584-588).
basalt	Pliocene Moraga andesite and basalt quarried since mid-1940's near Orinda in 1200 t.p.d. plant, for aggregate and road rock.
sandstone	Miocene sandstone with conglomerate and sea shells, (San Pablo group) quarried from at least three localities near Pacheco and Walnut Creek for local use as fill and road rock in 1940's; one operation active 1951.
	Franciscan sandstone quarried in at least six large pits along west flank of Berkeley Hills at Stege, El Cerrito, Berkeley Park, for aggregate, fill, roadrock, riprap. Inactive largely because of housing developments since about 1930. 1500 t.p.d. quarry at Pt. Richmond continuously active since 1907, and 1000 t.p.d. operation south of Clayton active continuously since 1947, both mainly for aggregate.
serpentine	Franciscan serpentine quarried briefly in 1947 south of Clayton, for aggregate.
undetermined	Undetermined type of rock quarried since 1953 at Orinda for crushed stone.
Marin County	(Ver Planck 1955, pp. 237-251).
basalt	Pliocene Sonoma volcanics andesite crushed for aggregate near Novato, starting 1954, at former paving block quarry.
sandstone	Franciscan sandstone quarried prior 1920 from at least 6 localities near Larkspur, Kentfield, San Rafael, San Anselmo, and Fort Barry, for dimension stone and crushed stone. Riprap quarried at Bodega Bay about 1950. Two large operations active in 1955, at Greenbrae (since 1925) and San Pedro Pt. (since 1945), have total capacity of about 10,000 t.p.d. of aggregate, riprap (jetty stone), ballast.
conglomerate	Cretaceous (?) Novato conglomerate quarried near Black Pt. since 1954; crushed and washed into component sand and gravel for aggregate, fill.
chert	Franciscan chert quarried at Black Mtn. prior to 1953, near San Rafael since 1893, and near Las Gallinas prior to 1915; for aggregate, paving blocks, fill.
Napa County	(Davis 1948, pp. 184-188; Averill 1929, pp. 238-242).
basalt	Pliocene Sonoma volcanics quarried continuously since 1921, is one of the State's most productive pits south of Napa for aggregate, riprap, ballast, road base, and fill. Also quarried east of Napa for aggregate, road rock since prior to 1929. Several basalt and trachyte tuff quarries near St. Helena formerly yielded dimension stone and byproduct crushed stone.
sandstone	Unidentified (Franciscan ?) sandstone obtained in early 1900's near Napa, Monticello, Rutherford, Pope Valley for local uses as dimension stone and crushed stone.
San Francisco County	(Laizure 1929, pp. 244-245).
sandstone and chert	Franciscan sandstone, chert, and jasper quarried from dozens of localities in late 1800's, and early 1900's for ballast, macadam and aggregate, and rubble (fill). All worked out or forced to close by expanded housing developments long before World War II.
San Mateo County	(Davis 1955, pp. 430-439; 448-455).
granite	Jurassic (?) Montara quartz diorite quarried from several medium-sized pits near Montara and Half Moon Bay intermittently for many years prior to 1951 for undetermined crushed stone products. Decomposed granite (deeply weathered Montara quartz diorite) quarried intermittently from at least three localities near Montara and Half Moon Bay for fill and road construction.
sandstone (basalt)	Franciscan sandstone quarried from at least 10 pits near Daly City, Brisbane, Millbrae, Burlingame, San Mateo, and Redwood City, for aggregate, ballast, and fill prior to World War II; four quarries near Brisbane, Millbrae and west of Redwood City active in 1955.
	Lower Miocene Vaqueros limey sandstone quarried in one locality north of Half Moon Bay about 1910-1920 for road rock.
carbonate rock	Pliocene Merced sandstone, shale and conglomerate quarried near Millbrae for S.F. Airport fill, 1946-1947.
	Franciscan (Calera) limestone obtained from two operations at Rockaway Beach (one active 1910-1919, 1942-present (1955); the other active (1944-52) for riprap, aggregate, railroad ballast, road base. Also quarried at two localities near Crystal Springs Lake (one active prior 1951; the other still active in 1955) for aggregate, road rock. Associated chert makes portions of the Calera limestone potentially reactive with portland cement, hence most is used with bituminous binder.
conglomerate	Upper Cretaceous conglomerate with some sand and shale, quarried intermittently for many years near Pescadero for road rock.



Table F. Principal sources of crushed and broken stone in California, by stone-producing districts.—Continued.

SAN FRANCISCO BAY AREA—Continued  
San Mateo County—Continued

greenstone basalt	Franciscan basalt and diabase, largely altered to greenstone, quarried in at least 5 intermittently active pits near Woodside, Sharp Park and Belmont for many years, mainly for fill. Sandstone, chert and shale are commonly associated.
chert	Miocene basalt, somewhat altered, quarried near San Carlos in 1947 for housing tract fill. Franciscan chert, intimately fractured, quarried intermittently from at least 4 localities near San Mateo Pt. and Belmont for many years mainly for fill.
Santa Clara County	(Davis and Jennings 1954, pp. 371-376; Crittenden 1951, pp. 64-65, plate 2).
granite	Jurassic gabbro and diorite, mixed with serpentine, quarried intermittently since prior to 1895 at Oak Hill for riprap and coarse aggregate.
basalt	Miocene basalt quarried at several locations west of Stanford campus for many years, used for road construction. Residential development has led to virtual cessation of quarrying since 1950.
carbonate rock	Franciscan (Calera) limestone produced at Permanente since 1939, mainly for cement, sugar rock; off-specification material crushed for use as fill, railroad ballast, road material.
sandstone	Franciscan sandstone ("quartzite") quarried near Saratoga since 1908 at county's oldest quarry (1200-2000 t.p.d.) for road materials. Small quarry in Halls Valley intermittently active for road material. Miocene Temblor sandstone obtained from small quarry near Calaveras Reservoir for riprap. Mio-Pliocene Purisima sandstone, rather soft, obtained in minor tonnage at basalt quarries west of Stanford campus, mainly for fill.
shale, chert	Miocene Monterey banded chert-and-shale quarried from at least 13 localities along the west flank of the Diablo Range for many years for fill and road materials.
conglomerate	Lower (?) Cretaceous Oakland conglomerate quarried intermittently for many years from at least 6 localities along the west base of the Diablo Range for use as road base and fill. Pleistocene Santa Clara conglomerate quarried near Stevens Creek dam for use as fill; 300-400 t.p.d. operation in 1952.
serpentine	Franciscan serpentine, in part silicified, and commonly occurring with shale, quarried in at least 4 localities near Morgan Hill and Los Altos for use as dam riprap, fill, drain rock and road base; 2 quarries active in 1954.
undetermined	Undetermined type of stone quarried for unspecified crushed stone usage at two localities near San Jose and Los Gatos.
Sonoma County	(Honke and Ver Planck 1950, pp. 110-113).
basalt	Pliocene Sonoma volcanics (basalt, andesite, and tuff) quarried in several dozen localities near Cloverdale, Healdsburg, Guerneville, Occidental, Santa Rosa, Bloomfield, Cotati, Sonoma, and Petaluma, for use as aggregate, road metal, sub-grade, fill. Many of these quarries intermittently active, some since early 1900's; five operators active in 1953.

## CENTRAL-SOUTHERN COAST RANGES

Monterey County	(Laizure 1925, p. 53).
granite	Pre-Franciscan Santa Lucia granite obtained from several small quarries near Monterey Bay for harbor projects, riprap, since World War II. Minor tonnage of decomposed granite also produced for road construction, fill.
carbonate rock	Gabilan limestone (dolomite), pre-Santa Lucia granite, quarried at Natividad since 1942, mainly for making magnesium; large tonnage of crushed dolomite also sold for roofing granules, poultry feed supplement, and white aggregate.
San Benito County	(Averill 1947, pp. 49-50, 60; Allen and Fowle 1946, pp. 77-81).
granite	Pre-Franciscan Santa Lucia granite, fractured by San Andreas fault movements, obtained from one of the State's largest quarries at Logan, active continuously since 1900 for use as aggregate, railroad ballast, filter medium, poultry grit, drain rock and road material. Small quantities of decomposed Santa Lucia granite quarried intermittently from at least two quarries near Highway 101 for local use as road material and fill.
carbonate rock	Gabilan limestone (and dolomite), pre-Santa Lucia granite, quarried intermittently since 1915 at several localities near Vineyard, about 8-10 miles south of Hollister, for unspecified purposes. Relatively minor tonnages of crushed carbonate stone sold as by-product for roof granules, poultry feed supplement and other uses.

## LOS ANGELES AREA

Kern County	
granite	Jurassic granitic rocks quarried in small operations near Tehachapi and Jawbone Canyon for roofing granules since 1950.
tuff	Miocene Kinnick and Bopesta formations near Tehachapi and Jawbone Canyon, and Rosamond formation, in Rosamond Hills, yield related minor tonnages of highly colored tuff and tuffaceous sandstone for roofing granules, at about a dozen localities, mainly since 1950.
carbonate rock	Undetermined carbonate stone quarried in small quantities near Inyokern for roofing granules in 1954.
Los Angeles County	(Gay and Hoffman 1954, pp. 526-553).
granite	Granitic rock, mostly of Mesozoic age, quarried at two large pits in San Gabriel Mountains for flood control dam riprap, 1936-1940; quarried prior 1940 near Acton and Pasadena for railroad ballast; quarried prior 1900 near Hollywood and Sunland for aggregate and fill. Small tonnage quarried near The Oaks in 1955 for roof granules; quarried intermittently at several localities for road material. Decomposed granite quarried near Pacoima, in Santa Monica and San Gabriel Mountains, in Verdugo Hills, and Sierra Pelona at many intermittent operations for fill and road base. Pleistocene La Habra conglomerate, mainly decomposed granitic debris, quarried at 4 large operations near Montebello for decomposed granite in 1950's.
basalt	Miocene basalt, somewhat altered, quarried at large pit in Palos Verdes Hills for many years for dike rock, fill in harbor installations, and road base. Miocene andesite quarried from at least 4 large pits on Santa Catalina Island at various times since 1900, barged to mainland for riprap, fill and various harbor construction purposes. Oligocene (?) Vasquez basalt, somewhat altered, quarried in two localities near Little Rock prior to 1935 for minor tonnage of roofing granules; in one small pit near Vincent, prior World War II for soil additive; and in several small pits north of Vincent since 1955 for roofing granules.
carbonate rock	Paleozoic (?) limestone quarried in several small pits near Largo Vista, Pearblossom for roofing granules about 1949-1952, several small operations near Pacoima Dam in 1940's for poultry feed supplement and roofing granules. Paleocene Martinez limestone quarried in Santa Ynez Canyon intermittently since 1928 for minor tonnage of riprap, road base, and stone for construction projects.
sandstone	Pleistocene Lomita marl quarried in at least 2 localities in Palos Verdes Hills for soil additive mainly prior to World War II. Upper Cretaceous Chico sandstone quarried from several pits near Chatsworth in early 1900's, mainly for building stone, but large tonnage used for riprap, San Pedro harbor breakwater stone, railroad ballast. Miocene Topanga (?) sandstone-conglomerate quarried intermittently for many years in Santa Ynez Canyon for riprap and building stone.
serpentine	Mesozoic (?) serpentine quarried in large pit on Santa Catalina Island in 1954-1955 for barge haul to mainland for harbor projects.
conglomerate	Mesozoic (?) Catalina schist (metaconglomerate) quarried in one of the State's largest quarries, at Pebbly Beach, Santa Catalina Island, for many years; barged to mainland for riprap and harbor uses.



Table F. Principal sources of crushed and broken stone in California, by stone-producing districts.—Continued.

## LOS ANGELES AREA—Continued

## Los Angeles County—Continued

shale.....	Miocene Modelo shale, very diatomaceous, quarried near Sunland since 1950, and pulverized for insecticide carrier.
soapstone.....	Oligocene (?) Vasquez silicified siltstone quarried in upper Agua Dulce Canyon since 1954 for roofing granules.
tuff.....	Pre-Cambrian (?) Pelona schist (soapstone) quarried near Acton since 1935 and pulverized for various uses as filler.
	Miocene Mint Canyon tuffaceous sediment quarried near Newhall since 1950 and pulverized for chinchilla dust; also altered volcanic ash quarried in Sand Canyon and processed for use as roofing granules.

Orange County.....	(Tucker 1925, pp. 69-71).
"granite".....	Pliocene or Pleistocene terrace deposits, consisting largely of weathered granitic rock, quarried east of Olive to obtain decomposed granite for fill, road base.

Riverside County.....	(Tucker and Sampson 1945, pp. 166-167).
granite.....	Cretaceous Woodson Mountain granodiorite obtained from large quarry in the south-central Jurupa Mountains, intermittently active since the early 1900's, mainly for harbor riprap (Long Beach breakwater 1925-29; Seal Beach 1944-49; Redondo Beach 1953, 1954). Similar granite quarried in one of the State's largest quarries, near Ormand siding west of Riverside, 1925-29 (2 million tons of riprap for Long Beach breakwater) and 1944-45 (700,000 tons for Seal Beach breakwater). Similar granite obtained at various times since 1900 near Box Springs Station; Quarry Hill near Arlington; Porphyry Siding near Corona; and LaSierra Hills near Norco for railroad ballast and riprap, and harbor riprap. Encroaching housing developments have restricted operations in several of these quarries since 1945. Poultry grit produced in small operation near Riverside since 1950. Decomposed granite obtained near Sunnymead for airfield construction during and since World War II.

carbonate rock.....	Paleozoic (?) or Triassic (?) limestone has been quarried at large quarries at Crestmore and the southern Jurupa Mountains since about 1900, mainly for cement, although lime and dimension stone have been produced at intervals. Since World War II, minor tonnages of roofing granules, poultry grit, agricultural stone, filler, and white aggregate have also been produced from these deposits and from several smaller deposits near Blythe, Palm Springs, Hemet, and San Jacinto.
basalt.....	Jurassic (?) Temescal Wash quartz latite porphyry obtained from one of the State's largest quarries, southeast of Corona, for manufacture of artificial colored roofing granules since 1948. Smaller quarry opened nearby in 1955 for drainage ditch riprap.

San Bernardino County.....	(Wright, et al., 1953, pp. 166-181, 190-197).
granite.....	Cretaceous Bonsall tonalite obtained from one of the State's largest quarries at Decezville, northwestern Jurupa Mountains, since prior to 1900 mainly for railroad ballast and riprap; yielded shoreline riprap for highway south of Ventura in 1955.
basalt.....	Pliocene (?) Red Mountain andesite quarried near Newberry and Baxter in 1955 for railroad ballast. Various highly colored volcanic rocks quarried in minor tonnages near Newberry, Midway, north of Barstow, and east of Lenwood for roofing granules since 1950.
carbonate rock.....	Paleozoic (?) or Triassic (?) limestone and dolomite obtained from large quarries near Colton, Oro Grande, and Victorville, almost continuously since the early 1900's, mainly for cement, but lesser tonnages crushed for fluxstone, glass manufacture, poultry grit, and cattle feed. Smaller operations have been active near Adelanto, Baldwin Lake, Sheep Creek, Van Dusen Canyon and Big Bear since 1950 for roofing granules; in Cave Canyon from 1906 to 1930 for sugar rock; near Chubbuck from 1925 to 1951 and near Victorville since 1924 for lime and various crushed limestone products; in Cushenbury Canyon since 1947, and near Hinkley in the mid-1940's for fluxstone. Minor tonnages of roof granules, poultry and stock feed, agricultural stone, filler and whiting produced at most of these operations.
volcanic cinders.....	Quaternary basaltic volcanic cinders quarried from Pisgah Crater and Dish Hill to provide a small tonnage of lightweight aggregate since the late 1940's; Mt. Pisgah cinders used for railroad ballast since 1955.
quartzite.....	Late Paleozoic Oro Grande quartzite quarried since 1939 near Oro Grande, mainly for special cement manufacture; large tonnage also crushed for use in refractories.

## WESTERN SIERRA NEVADA AREA

Amador County.....	(Carlson 1954, pp. 209-210).
granite.....	Upper Jurassic granodiorite and granite quarried intermittently as needed for road material at several localities near West Point Power House, near Pine Grove, and elsewhere in the central and eastern sections of the County.
carbonate rock.....	Paleozoic limestone quarried near Sutter Creek in 1945, mainly for sugar rock but fines were used for road material; small amount of by-product crushed stone from marble dimension stone quarries near Volcano, active 1910-1933, and near Plymouth, active prior to 1900.
slate.....	Upper Jurassic Mariposa slate quarried near Martell in 1941 in small operation for roof granules (?).
Calaveras County.....	(Logan and Franke, 1936, p. 235).
carbonate rock.....	Mississippian limestone quarried since 1926 near Kentucky House and Mokelumne Hill for cement, and undetermined by-product crushed stone; near Valley Spring for fluxstone prior to 1927. Small tonnage of yellow marble from near Vallecito crushed for terrazzo granules in mid-1940's.
greenstone.....	Amphibolite schist "greenstone" quarried near Angels Camp in mid 1930's for roofing granules and filler.
El Dorado County.....	(Logan 1938, p. 365).
carbonate rock.....	Carboniferous Calaveras limestone quarried in substantial tonnages since 1930 near Newcastle for glass manufacture and lime; at Diamond Springs since 1927 for lime, and filler; near Shingle Springs since the early 1920's for fluxstone, glass making, sugar rock and filler; at Cool-Cave Valley intermittently since the early 1900's for cement and lime manufacture, fluxstone and sugar rock, and continuously since 1947 for sugar rock, lime manufacture, fluxstone, and road material; near Auburn since 1910 mainly for cement manufacture but with increasing tonnage for sugar rock in recent years. Substantial tonnages of byproduct crushed limestone from nearly all of these localities used variously as crushed stone, especially since World War II.
slate.....	Jurassic Mariposa slate obtained from large underground quarry at Chili Bar since 1928, crushed for roofing granules and filler dust.
Fresno County.....	(Logan, Braun, and Vernon 1951, pp. 504, 528-531).
granite.....	Jurassic diorite quarried in at least 9 pits near Academy, mostly in early 1900's, for dimension stone; undetermined but minor tonnage of waste used as crushed stone for various purposes. Decomposed granite quarried near Friant, since 1940, and in Tivy Valley since 1920, intermittently as needed for roadbase, fill, and waterbound macadam surface.
carbonate stone.....	Paleozoic limestone quarried for lime manufacture at several localities in early 1900's; near Tollhouse in 1940's for poultry and cattle feed supplement, and fluxstone.
undetermined.....	Undetermined types of stone quarried near Piedra in 1953 crushed for macadam and railroad ballast.



Table F. Principal sources of crushed and broken stone in California, by stone-producing districts.—Continued

## WESTERN SIERRA NEVADA AREA

## —Continued

Lassen County	(Averill and Erwin 1936, pp. 443-444).
basalt	Basalt of undetermined age quarried west of Susanville since 1930's for road material.
Madera County	(Logan 1950, pp. 465-466).
granite	Jurassic granite obtained from several quarries near Raymond, two of them among the State's largest, for dimension stone, mainly from 1893 to 1942; waste granite from these quarries for many years crushed for road material.
Mariposa County	(Laizure 1928, pp. 146-152).
granite	Jurassic granite and granodiorite quarried intermittently in Yosemite Valley area as needed by Park Service for road material.
basalt	Jurassic diabase of Mariposa Mine dump in Mariposa crushed for road material in 1927.
carbonate rock	Mississippian limestone quarried at Jenkins Hill from 1927 to 1944 for cement manufacture; undetermined tonnage of byproduct crushed stone.
jasper	Jasper rock of undetermined age quarried at Jasper prior to 1927 for railroad ballast; discontinuously since then for roofing granules and unspecified special uses.
slate	Jurassic Mariposa slate quarried on small scale between Mariposa and LeGrand in the early 1900's; dump material later crushed for roofing granules.
Placer County	(Logan 1927, pp. 280-281, 285).
granite	Jurassic granite quarried at more than a score of quarries, several of them among the state's largest, at the Penryn and Rocklin districts, from about 1860 to 1920, mainly for dimension stone but large tonnages of railroad ballast, riprap and fill were also produced, in part as a byproduct. In 1950's one quarry yielded byproduct aggregate, ballast, and riprap at Rocklin.
carbonate rock	Mississippian limestone quarried in a dozen or more localities near Auburn, Clipper Gap, Applegate, Colfax, from about 1860 to 1916, mainly for lime and carbon dioxide manufacture, with minor tonnages for fluxstone and sugar rock, and undisclosed tonnages for various crushed stone uses.
Plumas County	
granite	Jurassic granite quarried in 1952-1953 near Tobin for railroad ballast.
Tulare County	(Franke 1930, pp. 442, 444, 445, 447, 463).
granite	Jurassic granite quarried near Porterville and Rocky Point from 1890's to 1930's, mainly for dimension stone; quarry waste employed in undetermined but minor tonnages for crushed stone. Decomposed granite quarried intermittently 14 miles northeast of Porterville for road material.
carbonate rock	Triassic and Paleozoic limestone quarried at several scattered localities in the Sierra Nevada and foothills, mainly for lime manufacture; minor production near Lemon Cove prior to 1933 for agricultural stone, paving material; sugar rock, fluxstone and oil well mud additive produced east of Lindsay prior to 1933.
Tuolumne County	(Logan 1949, pp. 76-80, 81, 82).
granite	Jurassic granite quarried near Soulsbyville for many years for unspecified uses as crushed rock; small dimension stone quarries near Sonora and Standard yielded undetermined tonnage of byproduct crushed stone prior to 1925.
carbonate rock	Mississippian Calaveras limestone and marble quarried at various times since about 1860 near Sonora and Columbia mainly for dimension stone and lime manufacture, but minor tonnages used for terrazzo granules, roof granules, filler dust, and poultry grit. The state's principal marble quarry at Columbia continuously active since 1942 for lime-burning material; smaller quarries nearby are the state's only current source of terrazzo granules.
slate	Jurassic Mariposa slate quarried near Hetch Hetchy Junction from 1931 to 1940 for roofing granules and filler dust.

## GREAT VALLEY AREA

Butte County	(O'Brien 1949, pp. 435-439).
carbonate rock	Carboniferous (?) limestone quarried on a minor scale in at least four localities near Big Bar, Forest River, Pentz, and Poe prior to 1930 for lime manufacture and undetermined crushed stone uses.
serpentine	Jurassic (?) serpentine quarried on small scale near Magalia in late 1940's for road and driveway material.
undetermined	Undetermined type of stone obtained in minor tonnages from mine dump near Magalia in late 1940's for aggregate and road material.
Colusa County	(Logan 1929, pp. 299-300).
sandstone	Upper Cretaceous Chico sandstone obtained from several large quarries just east of Sites prior to 1915, mainly for dimension stone, but undetermined tonnage of quarry waste used for road material.
Kings County	(Jennings 1953, p. 295).
shale	Miocene McClure shale, hard, dense, and siliceous, quarried in Big Tar Canyon and in Pyramid Hills prior to 1953 for unspecified crushed stone uses.
Shasta County	(Averill 1939, pp. 170-171).
carbonate rock	Triassic Hoselkus, Devonian Kennett, and Permian McCloud limestones quarried from at least 5 localities in the Shasta Dam area, principally prior to 1927 for lime manufacture and fluxstone; undetermined, but minor tonnage for crushed stone purposes. Large tonnage used in Shasta Dam in early 1940's.
Solano County	(Laizure 1927, pp. 212-213).
basalt	Lower Pliocene Sonoma (?) volcanics basalt quarried near Cordelia 1875-1895 for paving blocks, since then for aggregate, fill and riprap.
carbonate rock	Travertine of undetermined age quarried near Fairfield prior to 1950 for fluxstone, road material, and aggregate; from 1902 to about 1910 for cement manufacture.
undetermined	Undetermined types of stone quarried at several localities, including Benicia, for macadam, riprap, and fill for many years; two operations in 1953.
Sutter County	
basalt	Pliocene and Pleistocene andesite quarried intermittently at Sutter Buttes for many years for road material.
Yolo County	(O'Brien 1950, p. 423).
sandstone	Cretaceous sandstone quarried mainly for dimension stone, at Devils Gate 1894-1908, undetermined but minor tonnages of waste used locally as crushed stone.



Table F. Principal sources of crushed and broken stone in California, by stone-producing districts.—Continued

## EASTERN SIERRA NEVADA AREA

Inyo County.....	(Norman and Stewart 1951, pp. 100-102, 112).
carbonate rock.....	Tertiary travertine quarried in Furnace Creek Canyon for small tonnages of terrazzo granules in late 1940's. Silurian and Devonian dolomite quarried intermittently near Keeler from 1888 to about 1930; from about 1915 to 1951 for fluxstone, stucco aggregate, mineral wool manufacture, poultry grit, terrazzo granules, and roofing granules.
quartzite.....	Ordovician Eureka quartzite quarried near Keeler in 1954 for use in superduty refractory bricks.
slate.....	Slate of undetermined age, quarried intermittently prior to 1948 near Keeler for flagstone, roofing granules, and filler dust.
volcanic cinders.....	Quaternary cinder cone volcanic fragments quarried in at least 3 pits near Little Lake since the late 1940's, mainly for light-weight aggregate blocks, but large tonnages also used for railroad ballast, roofing granules and soil conditioner.

## SAN DIEGO AREA

San Diego County.....	(Tucker and Reid 1939, pp. 42-45, 49-51; Hoppin and Norman 1950).
granite.....	Jurassic granitic rocks quarried at about 20 localities near Vista, Escondido, and Lakeside, at various periods from about 1888 to the present (5 operations active 1952-1953). Mostly used for dimension stone, but large tonnages used about 1900 for rubble and riprap for breakwaters and dams, and about 1910-1920 for paving blocks. One riprap producer in 1952 in Escondido. Minor tonnages of quarry waste sold for crushed stone. Jurassic felsitic intrusive rock quarried near Lemon Grove in 1920's and 1930's for aggregate.
basalt.....	Jurassic (?) Black Mountain andesite quarried in 1953 in Mission Gorge for Mission Bay breakwater riprap.
carbonate rock.....	Paleozoic (?) limestone quarried on small scale in early 1950's near Alpine for roofing granules; lime and cement manufactured briefly and in minor tonnages at several localities in 1800's.
greenstone.....	Rhyolitic and other greenstones of undetermined age quarried in at least 3 localities near Rancho Santa Fe since 1930's for roofing granules.

**Crushed Limestone and Quartz.** The main uses of the monomineralic rock types limestone, dolomite, vein quartz, and quartzite are discussed in sections on those commodities. As they are crushed in most of their applications, either physical or chemical, they are briefly tabulated below as special types of crushed and broken stone. Other types of rock may be employed in many of the following uses either in place of, or in conjunction with the monomineralic rocks.

*Uses of crushed and broken limestone and dolomite \**

Use	Function	Remarks and references
Agriculture: soil additive	Physical and chemical, as soil conditioner.	See also sections on phosphates; gypsum and gypsum; also Bowen 1951, pp. 123-127.
Stock, poultry feed	Chemical, as supplemental source of calcium for milk cows and poultry.	
Ceramics	Chemical, as ingredient in whitewares and frits.	See also sections on clay; vein quartz and quartzite; specialty sands.
Chemical processes	Chemical, as acid neutralizer, and other uses.	
Cigarette urns	Physical, for clean, white color.	See also section on specialty sands.
Filler	Physical, clean, white. Chemical, inert.	
Fluxstone	Chemical, as blast and open-hearth furnace charge.	See also sections on iron industries; fluorspar.
Glass	Chemical, as ingredient.	See also sections on specialty sands.
Refractories	Chemical, as binder for refractory brick.	See also sections on quartzite and quartz; specialty sands; clay.
Whiting	Physical, for white color. (Chemical, for inertness).	

\* See sections on cement and lime, limestone and dolomite elsewhere in this volume.

The large tonnages of crushed and broken limestone and dolomite used for roofing granules are discussed above in this section. Relatively little crushed or broken limestone or dolomite is used for riprap, concrete aggregate, or railroad ballast in California, although such use is common in other states.

*Uses of crushed vein quartz and quartzite.\**

Use	Function	Remarks and references
Abrasives	Physical, as in sandpaper. Chemical, as ingredient of artificial abrasives.	See also sections on abrasives; specialty sands.
Ceramics	Physical and chemical, in whiteware bodies and frits, and as placing sand.	See also sections on clay; lime, limestone, and dolomite; specialty sands.
Chemical industry	Physical, as catalyst carrier in oil refining.	
Ferroalloys	Chemical, as ingredient.	See also sections on iron industries; specialty sands.
Filler	Physical, clean, white. Chemical, inert.	
Foundries	Physical, as ganister for furnace, ladle linings.	See also section on specialty sands.
Glass	Chemical, as ingredient.	See also section on specialty sands.
Refractories	Physical, as ingredient in refractory brick.	See also sections on clay; specialty sands.
Soluble silicates	Chemical, as ingredient.	See also section on specialty sands.

\* See section on quartzite and quartz elsewhere in this volume.

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## STONE, DIMENSION

BY HAROLD B. GOLDMAN

Stone production is among the oldest and largest of the mineral industries of California. Commercial dimension stone quarries were operated as early as 1854 at Monterey and Point Reyes (Blake, 1858, p. 281). Until the early 1900's the production of dimension stone, mainly for use in buildings, paving, and curbing, greatly exceeded that of crushed stone but since then the dimension stone output has dwindled while production of crushed stone has increased many fold. The development of the steel-frame buildings, which required comparatively little stone, and the introduction of concrete, which is much less expensive and more conveniently used than stone, combined to cause this decline.

In the rock products industry, the term "stone" is applied to blocks, masses or fragments of rock broken or quarried from their original massive ledges for commercial use (Bowles, 1939, p. 5). The term "dimension stone" is applied to natural stone that is cut to definite size and shape and includes cut, carved and roughhewn blocks of building stone, paving blocks, curbing, flagging, and cut and polished monumental stone.

The term "crushed stone" is applied to irregular rock fragments, which result from crushing and grinding, that are not of specific shape. Crushed stone, which is used as bituminous and portland cement aggregate, railroad ballast, riprap, and in many chemical, metallurgical and industrial processes, is discussed more fully under that heading elsewhere in this bulletin.

The total recorded production of dimension stone in California from 1887 to 1955 approximates 42 million dollars in value. In 1955, dimension stone valued at approximately \$690,000 was produced in the state. This stone was used principally for monumental and building stone. Rock types quarried in 1956 were granite, light-colored volcanics, siliceous limy shales, mica schist, slate and quartzite.

### CLASSIFICATION OF DIMENSION STONE BY USE

Dimension stone is subdivided by uses into building stone, monumental stone, paving stone, curbing, and flagging.

**Building Stone.** One of the principal uses of dimension stone is as a construction material. Included in this category is stone in any form that constitutes a part of a structure; for example, window sills, walls, steps, or fireplaces. Whereas building stone formerly was a basic construction material, its present function is largely ornamental. Building stone is marketed as rubble, rough building stone, ashlar, and cut or finished stone.

Rubble, the crudest form of building stone, consists of irregular rock fragments, each having at least one essentially flat face. The stone is usually shaped by hand. It is used as veneer on small commercial buildings, in private residences for walls, patios, fireplaces, and swimming pools. Rough building stones consist of rock masses that are rough-faced and of non-uniform shapes. This stone also is usually shaped by hand.

"Ashlar" is a term applied to small rectangular blocks with sawed, planed, or naturally cleft surfaces.

Ashlar blocks are used similarly to brick and are laid so that several sized blocks are fitted together to make a wall having irregular or unequally spaced joints. Figure 1 shows a common method of laying ashlar (after Bowles, 1939, p. 24). Ashlar is produced by using a block-splitting machine or by sawing.

Cut or finished stone includes cut blocks that are accurately sized and surface-tooled. The stone is used for ornamental purposes such as interior or exterior wainscoting, floor tile, steps, columns, baseboards, and various other ways.

**Monumental Stone.** Only the finest types of flawless uniform stone are used in the production of monuments. Monuments range from simple markers and headstones to elaborate and massive memorials. Stone used for this purpose must be of subdued color, take a good polish and exhibit a distinct contrast between carved and polished surfaces.

**Paving Stone.** One of the earliest uses for stone was for street and highway paving. Concrete and macadam have almost entirely replaced paving block for this purpose, although many stone pavements still give excellent service, particularly in areas subjected to heavy vehicular traffic. Only the more resistant rock types such as granite and basalt are suitable for paving stone.

**Curbing.** Curbstones are of two types, straight and corner. Corner cuts are curved and are more difficult to make, with more waste, than straight curbs. Hard and tough rock types such as granite and basalt are particularly adaptable for corner curbs where shocks from the wheels of vehicular traffic are especially intense.

**Flagging.** Attractively colored rock types that split easily into slabs are suitable for flagging. Flagging is used chiefly for walks, gardens and patios around small commercial buildings and residences.

### SPECIFICATIONS OF ROCK USED FOR DIMENSION STONE \*

Only a small portion of the rock that comprises the earth's crust can satisfy the exacting specifications for most dimension stone. Freedom from cracks and lines of

\* After Bowles, 1939, pp. 26-30.

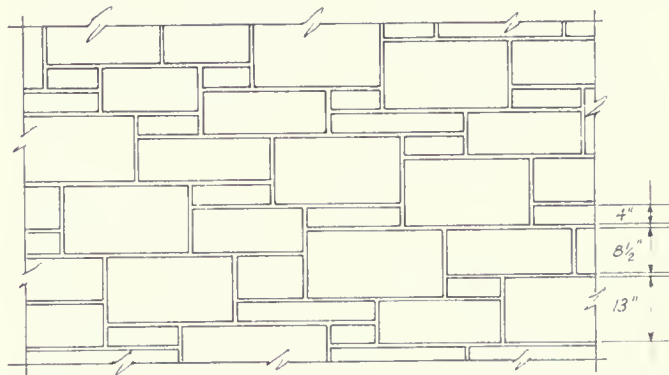


FIGURE 1. A common method of laying ashlar building stone.



weakness is essential. Uniform texture and grain size together with an attractive color are generally required. The rock must be free from such minerals as pyrite, marcasite, and siderite, which oxidize upon weathering to cause deterioration or surface staining. A rock that splits easily in one or two planes is desirable. Many rocks, particularly granites and sandstones, split in some directions with greater ease than in others. The direction of easiest splitting or the fracture system that makes splitting possible is called the "rift." A second and less strongly marked fracture system, generally at right angles to the rift, is called the "grain" or "run." The direction of splitting at right angles to both rift and grain is called the "hard way" or "head grain."

**Hardness and Workability.** The hardness of a rock is its resistance to abrasion and is directly related to the hardness and texture of its component minerals. For example, the principal minerals of granite—quartz and feldspar—are as hard or harder than steel and occur as closely spaced, commonly interlocking grains. Therefore, granite is difficult to tool. Grains of a sandstone consist of quartz and feldspar which are hard as steel, but the workability of sandstone depends mostly upon the nature of the cementing material and degree of induration. Hardness is relatively unimportant in stone used for exterior or interior walls as such stone is not subjected to wear. Conversely, stone that is used for floor tile, stair tread, paving block or curbing, should be hard enough to resist abrasion.

**Texture.** The texture of a rock is a function of the size, arrangement, and uniformity of the constituent mineral grains. In cut and polished monumental stone, uniform texture is of prime importance. For building purposes, a non-uniform texture commonly is preferred. The trend in recent years is toward natural appearance in exterior building stone and non-uniformity of color or texture.

**Color.** The popularity of a particular building stone depends largely on attractiveness of color and whether or not the color is currently fashionable. Red, green, buff, and gray-colored rocks are widely used for building stone. For monumental stone, rocks that show a marked contrast between polished and tooled surfaces are used, with color a secondary consideration.

**Strength.** The strength of ordinary dimension stone in structures generally far exceeds the requirements of safety. A stone that will sustain a crushing strength of 5,000 pounds per square inch is considered satisfactory for ordinary use as a construction material (Bowles, 1939, p. 28). In primary ornamental dimension stone, the strength factor is less significant.

**Porosity and Specific Gravity.** Porosity, expressed as the ratio of pore space to the total rock volume, varies with the rock type. Porosity ranges from 0.5 to 5 percent in limestone; is less than 1 percent in marble, granite and slate; and ranges from 10 to 20 percent in sandstone. Porosity affects durability by permitting water to penetrate into the rock, thereby causing mineral solution or disintegration by expansion during freezing and thawing cycles. A low porosity and absorption is, therefore, desired in a dimension stone.

Specific gravity is the weight of a stone compared to the weight of an equal volume of water. The specific gravity of the common rock types ranges from 2.2 to 2.8; the weight per cubic foot ranges from 140 to 180 pounds depending upon the weight of the constituent minerals and the porosity.

**Durability.** The durability of a rock may be judged by examining the effects of weathering on outcrops or old structures in which the stone was used. Laboratory tests such as freeze-thaw, absorption, and sodium sulfate soundness can also be employed to determine durability.

## ROCK USED AS DIMENSION STONE IN CALIFORNIA

### Granite and Related Rocks

Granite, defined geologically, is a medium- to coarse-grained crystalline rock that consists essentially of potash feldspar, subordinate sodic feldspar, and quartz. In the stone industry the term "granite" is used more broadly to refer to various intrusive igneous rocks with granitic textures, and even some metamorphic rocks with gneissic textures. Such igneous rocks as syenite, granite, granodiorite, quartz monzonite, diorite and gabbro, which range in color from light to dark and in composition from acidic to basic, commonly are referred to commercially as "granites."

Granites are the hardest of all of the rocks that are in common use as dimension stone and are the most difficult and expensive to quarry and shape into finished forms. The suitability of a granite for dimension stone is governed mainly by physical properties (texture, color, and hardness), and structural features (joints, fractures, rift, grain, sheeting, dikes, knots, and hair-lines). Chemical composition is of little economic significance.

Unweathered granites are generally hard, strong and resistant to chemical attack. Most bodies of granite are remarkably uniform in grain size and homogeneity of grain distribution. Granite for dimension stone must be capable of taking a smooth, long-lasting polish and should be free of deleterious minerals, such as the iron sulfides, which cause deterioration and unsightly staining upon oxidation. Although granites are hard, they vary in brittleness and toughness, depending upon the degree with which the mineral grains are interlocked.

Granite is strong and durable and will stand exposure to weather for many years before showing signs of decay. This period ranges from 75 to 200 years depending upon the location and climate (Ries, 1937, pp. 102-130).

The quarrying of granite is guided largely by the spacing and arrangement of joints and sheeting planes. The most easily quarried masses contain two straight major joint sets 10 to 30 feet apart intersecting at right angles. The presence of a defined rift and grain is vital to the ease with which the stone may be split. Sheeting planes are partings that generally parallel the exposed surface of a granite mass separating the mass into sheets or layers much like the skin of an onion. They are most advantageous where spaced at distances of 10 to 30 feet. Dikes, knots, (dark inclusions or segregations) and hair-lines (veinlets or discoloration along fractures) mar the appearance of a stone and are unwelcome in quarries





FIGURE 2. Bank of California building, California and Sansome Streets, San Francisco, built with granite from Raymond district, Madera County. Photo by Bob Lackenbach, courtesy of Cal-Pictures.

because of the time and labor spent in avoiding and removing them. Hairlines are unrecognizable on rough surfaces but are visible and objectionable on polished surfaces. The dikes, which are tabular bodies of igneous rock cutting across the granite, range in width from a fraction of an inch to several feet or more. Knots are either segregations of dark minerals in "spots" formed during cooling and solidification, or "inclusions" of foreign matter.

The principal uses of dimension granite, listed in order of production value, are monumental stone, building stone, curbing and paving block. A comparatively new use for granites is as surface plates which consist of accurately polished blocks with almost perfectly flat surfaces. They are used, instead of cast iron or steel, as precision tools for checking of instruments, small assemblies, parts, and any engineering work that requires a smooth flat surface. Only the dark, basic types such as norite and gabbro have been used for surface plates in California. Granite for this purpose must have a low absorption, low compressibility, and a low coefficient of thermal expansion (Merriam, 1955, p. 100). Granite is also one of the common rock types used as crushed stone in California (see section on crushed stone in this volume).

Granite has comprised approximately 75 percent of the total dimension stone produced in California from 1887-1955. The total recorded production of granite for this interval approximates 32 million dollars (Averill et al., 1946, p. 92). In 1955, dimension stone granite worth \$250,000 was produced in the state.

Granitic rock underlies about 40 percent of California's land area and occurs mostly in the large bodies known as the Sierra Nevada and southern California batholiths, and in smaller bodies exposed in the Klamath Mountains and in the desert regions of the state (see crushed rock section in this volume). Granite has been quarried for dimension stone along the western margin of the Sierra Nevada batholith in Fresno, Madera, Sacramento, and Tulare Counties; and along the western and northern borders of the southern California batholith in Riverside, San Bernardino, and San Diego Counties. Because these major granitic bodies occupy mountainous areas, the main granite quarries lie on the flanks or in outlying smaller masses, as close as possible to major transportation routes to centers of consumption. Not all the exposed granitic rocks are suitable for dimension stone. In some areas the rock is deeply weathered or fractured. For example, none of the granitic rocks of the Santa Monica or San Gabriel Mountains in southern California have proved free enough of shattering and weathering to be quarried as dimension stone.

*Quarries in the Sierra Nevada Batholith.* Quarries in the Sierra Nevada batholith have yielded approximately half of the granite dimension stone and about 40 percent of all the dimension stone produced in California. The most productive districts have been at Raymond, Madera County; Rocklin, Placer County; and Academy, Fresno County. Smaller areas were active at Folsom, Sacramento County; Porterville, Tulare County; Nevada City, Nevada County; and Susanville, Lassen County. The quarries have been located mainly



on low rounded outcrops in the foothill area where the granite was exposed at the surface or as residual boulders. The periods of greatest activity were from 1889-1895, 1903-1905, 1920-1930.

The principal source of granite in California has been the Raymond district in Madera County. This district, which was active mainly from 1888 to about 1943, has a total production valued at about 10 million dollars (Logan, 1950, p. 456). Granite is quarried from a broad exfoliated dome about 700 feet in diameter. The dome is comprised of a remarkably uniform, pale-gray biotite quartz diorite, that splits easily with a straight even grain. The sheeting planes, which are from 2 to 25 feet apart, parallel the surface of the dome and form the principal plane of parting. A well-defined rift trends northeast and the grain northwest. The rock has been removed at two large quarries and several small ones, all on the west side of the dome.

The largest quarries, the Raymond Granite Co. (Knowles), and the McGillivray (McClellan), are about 300 feet long and 25 to 40 feet high. The quarry floor, which is the sheeting plane, is inclined 20 to 30 degrees to the northwest. The stone was quarried, with hand and steam drills, by drilling and wedging along the rift and drilling and blasting along the grain. Quarrying began in 1888 and continued at a constant rate until the depression years of the 1930's. In 1914, from 400 to 500 men were employed at these quarries. The peak year was 1925 when granite valued at \$1,358,410 was produced for public building construction in Los Angeles (Logan, 1950, p. 456).

Since the 1930's, small amounts of granite have been produced in the Raymond district for use as monumental stone. Here, in 1950, a quarry was opened and a finishing plant constructed to supply building stone for State buildings in Sacramento. The operation, which lasted for about 3 years, was financially unsuccessful and the completely-equipped plant is now idle. The oldest and most productive of the quarries, that of the Raymond Granite Co., was acquired in 1953 by the Cold Spring Granite Co. of Minnesota which in 1956 was installing new wire saws, gang saws, polishers, and a 140-ton steel derrick. About 12 men will be employed to produce monumental stone principally for shipment eastward.

Granite similar to that quarried at Raymond has been quarried in Placer County from an area that extends from Rocklin to Newcastle. Since 1863, granite valued at well over 3 million dollars has been produced from this district (Logan, 1927, p. 236). Here, a triangular-shaped portion of the batholith, approximately 20 miles long and 5 to 10 miles wide and extending from Folsom in Sacramento County to northeast of Lincoln in Placer County, has been exposed by erosion. Quarrying has been confined to the gently rolling plain, approximately 6 miles long and 1 to 2 miles wide, that extends from Rocklyn to Penryn. The granite occurs as massive exposures with a light overburden, and as residual surface boulders. The stone is a uniform pale-gray quartz diorite that splits easily into slabs 10 to 20 feet long and takes a high polish. East of Penryn a small outcrop of black hornblende gabbro also has been quarried for monumental stone.

Quarrying began in 1863 at Penryn, Loomis, and Rocklin. The quarries were ordinarily worked by 2 or



FIGURE 3. Cold Spring Granite Company quarry in the Raymond district, Madera County. The sheeting planes that parallel the surface facilitate quarrying.

3 men and consist of rectangular pits several of which are 100 or more feet deep. The main period of activity was from 1864 to 1890. Twenty or more quarries were operating in 1910. The last large order for building stone was in 1920 when granite valued at \$212,625 was produced at Rocklin for the Bank of Italy building in San Francisco. In 1956, only one quarry, that of the Union Granite Co., Rocklin, was being worked. This company which has been active for over 30 years, produces from a rectangular pit approximately 150 feet wide, 500 feet long, and 150 feet deep. Blocks are removed by channeling (drilling closely spaced rows of holes and cutting out core between) and lifted directly into a finishing plant at the edge of the quarry. The stone is sawed, polished and engraved for use as monuments. Waste is used as crushed rock (see section on crushed and broken stone in this volume).

Granite dimension stone valued at more than \$650,000 has been produced in the Sierran foothills 1 mile northeast of Academy in Fresno County (Logan et al., 1951, p. 504). In this district a dark-colored augite gabbro-diorite crops out as residual surface boulders and as massive ledges underlying low rounded hills. Nine quarries in all have been worked in a 100-acre area. In 1903, the Academy Granite Company began operating what is now the oldest and largest quarry. This company subsequently consolidated under the name of Clovis Quarries and in 1956 was still active. The stone is removed from a quarry opening about 100 feet high and 50 feet wide. A major joint system parallels the face of the quarry and blocks are removed by undercutting by means of drilling and blasting. Residual boulders also are found in the quarry and are moved to the quarry floor where they are wedged to size. Three to four men are ordinarily employed. Blocks are trucked 11 miles to a dressing and polishing plant at Clovis where they are finished, principally as monumental stone. Larger blocks are shipped by rail to surface plate manufacturers.



Granite valued at \$740,000 has been produced in Tulare County from three quarries in the foothills east of Porterville and Exeter. A dark-gray "black granite" (gabbro-diorite), composed of andesine feldspar, augite and biotite; and a pale-gray biotite granite occur as residual boulders and in massive exposures that comprise low hills. Production started in 1889 at the Rocky Point quarry east of Exeter. At Success the Raymond Granite Co. has intermittently quarried "black granite" blocks by channeling methods, but this operation was shut down in 1953. The blocks were shipped to the Raymond Granite Company's finishing plant at Raymond.

The oldest granite building stone quarries in California are at Folsom, Sacramento County. They were opened in 1856 to provide stone for construction projects in San Francisco. The main periods of activity of the Folsom quarries were from 1894 to 1911 and 1921 to 1931 when granite valued at about \$675,000 was produced (Carlson, 1955, p. 127). The quarries exist in massive exposures at the southernmost extremity of the granitic mass in which the Placer County quarries are located.

Two small granite quarries at the northern end of the Sierra Nevada batholith in northeastern California have been operative since 1915. The Greig quarry south of Susanville, Lassen County, and the Netz quarry, Nevada City, Nevada County have consistently produced small amounts of paving and monumental stone from granite boulders.

*Quarries in the Southern California Batholith.* In San Diego, Riverside, and San Bernardino Counties the various bodies of granitic rock, known collectively as the Southern California batholith, are sources of dimension stone. The production of granite in San Diego County from 1898-1955 amounted to \$1,943,000, approximately 6 percent of the total granite production in the state for this interval. During the period 1950-55, this county has contributed about one-third of the granite dimension stone produced in California. Two types of granite have been quarried in the county, a pale-gray granodiorite and a "black granite," which includes such rock species as hornblende gabbro, norite, and quartz-biotite gabbro. The "black granite" is in demand for use in monuments and building fronts because of its pleasing black color, fine-grained texture which permits a high polish, and its resistance to weathering. However, the "black granite" is unusually hard and tough and therefore more costly to quarry and finish than most other California granites.

Most of these "black granite" quarries are in residual boulder deposits, whereas the light-gray granite is quarried mainly from massive rock. Distinct joint sets and a poorly developed sheeting structure characterize the massive exposures. The joints intersect at right angles and are spaced from 1 to 10 feet apart. The sheeting surfaces dip gently and generally are parallel to the slope of the land surface and are irregularly spaced from 6 inches to 6 feet apart. Such features are rarely observed in residual bouldery deposits. The boulders have formed chiefly from weathering through expansion and subsequent breaking apart by disintegration. A more extensive description of the occurrence of the "black granite" is provided in a recent publication (Hoppin and Norman, 1952).



FIGURE 4. Residual boulders of "black granite" in quarry of Escondido Quarries, Escondido, San Diego County. Boulders are removed to floor for drilling and blasting.

The principal dimension stone districts in San Diego County are near Lakeside, Escondido, and Vista. Since 1888, more than 40 quarries have been opened. Fifteen quarries have been active for various periods since 1953, and seven were being worked in 1956. In 1955, granite valued at \$92,180 was produced in the county. The most productive operation in 1956 was that of Escondido Quarries near Escondido. Here, boulders of "black granite" are removed from a quarry 70 feet high and 125 feet long. The boulders are rolled to the quarry floor and split into rough blocks by drilling and blasting with black powder. The crude blocks are cut by gang saws or a four-strand wire saw into slabs which are shipped to the finishing plants of Pacific Cut Stone at Alhambra, Los Angeles County, and Clovis Quarries at Clovis, Fresno County. The stone is used for monuments and for making surface plates.



FIGURE 5. Boulder deposit of "black granite" in Valley Granite Company quarry, Escondido, San Diego County. The boulders, which range from 6 to 8 feet in diameter, are drilled and blasted in place.



Most of the granite dimension stone produced in Riverside County has been quarried within 10 miles of Corona and Riverside. The remainder has been obtained from two quarries near Temecula. Four of the larger dimension stone quarries in the county—one at Casa Blanca, and others near the settlements of Noreo, Porphyry, and Temecula—have been virtually inactive since the early 1900's. Three or four large quarries in Riverside County, as well as the Decezville quarry in the Jurupa Mountains of San Bernardino County, were worked for dimension stone in the early 1900's and since then have been intermittently active as sources of large riprap stone for harbor projects (see section on crushed stone).

About a half dozen small quarries near Victorville and Oro Grande were active in the late 1800's and early 1900's, yielding building, monumental, paving, and curbing stone. This stone, much of which was obtained from boulders, was used locally and some was shipped as far as San Francisco. Little or no production of granitic stone has been reported in this district since prior to 1906. Two small quarries in deeply jointed rock about 10 miles northeast of Lucerne Valley have been active intermittently since the mid-1930's, yielding moderate tonnages of granitic building monumental stone which has been used primarily in the Los Angeles area.

#### Sandstone

Sandstone is a consolidated sedimentary rock composed mostly of mineral or rock fragments that range in size from  $\frac{1}{16}$  mm. to 2 mm. The most common cementing materials are iron oxide, calcite, silica, and clay. The predominant mineral grains in most sandstones in California are quartz, feldspar, and mica. Some sandstones are composed almost entirely of quartz grains; other sandstones contain 33 percent or more of fragments of dark-colored rocks and minerals and are known as graywacke.

The usefulness of a sandstone as dimension stone depends largely upon the nature of the cementing material and degree of cementation. All gradations exist between poorly cemented "sand" through sandstone to the dense, hard rock known as quartzite. Only the harder types of sandstones are used as dimension stone. As some are cemented more firmly in certain parts than in others, they contain hard and soft spots, an undesirable feature. Most of the sandstones that are strong enough for a good building stone and soft enough to be economically quarried and dressed contain iron oxide or clay as the principal cement.

Permanence of color is desired in a sandstone. The deeper shades of red, brown, yellow or buff are generally permanent as they are caused by the stable iron oxides—limonite or hematite. Blue or gray sandstones may contain ferrous sulfides or ferrous carbonates which, upon exposure, will oxidize to the more stable forms and gradually assume buff or red colors (Bowles, 1939, p. 69). Uniformity of color is not essential, as varicolored rocks produce pleasing architectural effects. Uniformity in grain size, however, is a very desirable feature in sandstone.

The ease with which sandstone can be worked, its variety of pleasing colors, and its ability to harmonize with brick and other building material makes it one of

the most desirable of the building stones. The principal uses of dimension sandstone are for building stone, flagging, and curbing. An estimated 4 million dollars worth of sandstone has been produced as dimension stone in California since 1887 (Averill et al., 1948, p. 92). No rock type classified petrographically as a sandstone has been produced as dimension stone in California since 1942.

Sandstone crops out predominantly in the Coast Ranges of northern and central California and the Transverse and Peninsular Ranges of southern California. Almost all of the dimension sandstone has been produced from Cretaceous formations.

The principal centers of past production were located at Sites, Colusa County; Graystone, Santa Clara County; Chatsworth, Los Angeles County; and Sespe Canyon, Ventura County. The main period of sandstone production extended from 1888-1919.

Probably the first dimension sandstone to be produced in California was quarried from sandstones of the Franciscan (Mesozoic) group at Angel Island in San Francisco Bay. The Angel Island quarries were active as early as 1865 and furnished building stone for construction in San Francisco.

The principal source of dimension sandstone in the state has been the Upper Cretaceous sandstones near Sites in Colusa County. From 1894 to 1914, these sandstones yielded about 1,186,000 cu. ft. of dimension stone valued at \$1,448,000 (Logan, 1929, p. 286). The Sites locality is in a belt of interbedded sandstone and shale that extends along the western margin of the Sacramento Valley from the northern boundary of Colusa County southward for 20 miles. In the vicinity of Sites massive sandstone beds, suitable for building stone, are exposed for a distance of 8 miles in a zone three-fourths of a mile wide. The beds range in thickness from 4 to 35 feet, dip approximately 50° to the northeast, and strike northwest. The stone has a blue-gray and buff color which weathers to light brown, is soft and has an even grain.

Three closely spaced quarries were opened on the east side of the sandstone-bearing belt, and were enlarged until each was approximately 250 feet long and 200 feet in maximum height. Blocks were quarried by drilling holes 2 to 3 feet apart and shooting with powder. The blocks were shipped by rail to finishing plants. This locality was worked steadily from 1901-1914. Since that time little or no stone was quarried, although occasional sales were made of stone previously quarried. Maximum production was in 1904 when stone valued at \$290,000 was produced (Aubury, 1906, p. 116). Most of the sandstone used in buildings in San Francisco, including the Ferry Building and the St. Francis Hotel, came from the Sites locality.

Another center of sandstone production in northern California was 9 miles south of San Jose in Santa Clara County. Here Cretaceous sandstones underlie an elongate area, 4 miles long and  $\frac{1}{2}$  mile wide, on the southwest flank of the Santa Teresa Hills (Davis and Jennings, 1954, p. 383). The beds range in thickness from 3 to 10 feet and dip at approximately 25° to the north. The stone is uniform in texture and color (buff) and soft enough to be easily carved. The largest operation was the Graystone quarry which was 100 feet high and 200





FIGURE 6. Inactive sandstone quarry of the McGilvray Stone Company at Sites, Colusa County. Quarry is about 150 feet in width. This quarry provided stone for many buildings in San Francisco, such as the Ferry Building and St. Francis Hotel.

feet long. Quarrying began here in 1866, and was most active from 1900 to 1905 when an output valued at half a million dollars or more was obtained. The stone was used in buildings in San Jose and to construct the buildings on the campus of Stanford University at Palo Alto. No production has been reported since 1905.

In southern California, large tonnages of sandstone were produced in the early 1900's from the Upper Cretaceous Chico formation which comprises the Simi Hills along the western margin of the San Fernando Valley near Chatsworth in Los Angeles County. Prominent massive sandstone beds, ranging in thickness from 20 to 25 feet and dipping approximately 20 to 25° to the north, occur in a belt, 15 miles long and 3 miles wide. The stone, an arkose, is blue-gray on fresh surfaces and weathers buff. It is fine-grained and very uniform in texture and color and splits readily. In the early 1900's five quarries were active in this area, but all were shut down by 1915, and no subsequent activity has been reported (Gay and Hoffman, 1954, p. 533). Blocks were quarried by hand drilling, blasting with black powder and split with wedges. The stone was used in churches, commercial buildings, and private residences in southern California.

In Ventura County an Oligocene sandstone, the so-called "Sespe Brownstone," was quarried in Sespe Canyon near Santa Paula. The sandstone is exposed at the crest of the "Cold Water antiform" and crops out in beds 10 to 20 feet thick. Two sets of nearly perpendicular joint planes divide the beds into rectangular blocks. Some of these blocks were quarried in place, but most of the quarrying was in blocks that had worked loose and rolled down the canyon. Several operators were active as early as 1888 and through the early 1900's (Aubury, 1906, pp. 142-144). No subsequent activity has been reported from this district. Small but significant amounts of dimension sandstone also have been produced in Amador, Contra Costa, Kern, Orange, San Bernardino, Santa Barbara, Shasta, and Siskiyou Counties.

### Limestone and Marble

To the petrologist marble is a crystalline limestone, but in the stone industry and in the present discussion the term "marble" is applied to any calcareous rock capable of taking a polish. Some marbles are composed almost entirely of carbonate minerals; others contain such impurities as silica and silicate minerals, iron oxide and iron sulfide minerals, and organic matter. Marble is commonly white, but the iron oxides impart colors of tan, red or brown, whereas carbonaceous matter causes a gray to black color. Verde antique is a greenish rock composed of serpentine mixed irregularly with calcite.

Marbles are tougher than most limestones, as grains of calcite in limestone usually are less firmly cemented together. Uniform hardness and high resistance to abrasion are desirable qualities in marbles to be used for floor tile, sills, or steps. Marble for exterior purposes should have a low porosity to prevent infiltration of water which may dissolve or discolor the stone. Marble to be used for monuments should present a distinct contrast between chiseled and polished surfaces.

Impurities, such as iron sulfides, silica and dolomite, should be avoided. The chief iron sulfides in marble—pyrite and marcasite—decompose when exposed to weathering, causing undesirable discolorations. Weathered outcrops of the deposit should be examined to notice such effects. Silica knots or bands differ in color and texture and detract from the appearance of marble. As silica is much harder than carbonate minerals, its presence retards channeling, drilling, or sawing, injuring tools. Because of this difference in hardness, a uniform finish is difficult to obtain on siliceous marble.

Alternating masses of dolomite and calcite also are undesirable in dimension stone marble, as they weather unequally and cause a nonuniform surface. The stone also may exhibit differences in texture, color and susceptibility to polish because of the presence of these two different minerals. Pure dolomite or intimate mixtures of dolomite and calcite is not to be regarded as inferior.

The principal uses of dimension marble are as building stone and monumental stone. Marble is also used as crushed stone (discussed under that heading elsewhere in this volume).

Despite its widespread occurrence in California, marble has been produced commercially in only a few localities; principally in Tuolumne, San Bernardino and Inyo Counties. From 1887 to 1946 the total recorded production of marble in California was valued at about \$3,588,000 (Averill, et al., 1948, p. 90).

The Columbia district near Sonora, Tuolumne County, has been the principal source of marble in California. From 1904 to 1942 this district yielded 255,000 cubic feet of marble valued at \$700,000. (Logan, 1949, pp. 51-53). Quarrying began here in 1860, and, from 1862 to 1866, thousands of tons were processed by a mill with 100 saws and four polishing machines. But with the erection in San Francisco of similar plants to handle marble from Italy and Vermont, the marble operations at Columbia and elsewhere in California were greatly curtailed. The Italian stone was brought as ship ballast to the Pacific Coast more cheaply than marble could be transported from California quarries 150 miles from market. The Columbia quarries, however, continued to





FIGURE 7. Inactive marble quarry of the Columbia Marble Company, Columbia, Tuolumne County. The cut faces are 6 to 8 feet high. Much of the interior marble used in buildings in California came from this quarry.

produce for a local market, and, with the building of the Sierra Railway in 1878, began again to supply the San Francisco market. The quarries were most productive from 1904 to 1914, and were intermittently active until 1942. The year of greatest production was 1910, when 27,600 cubic feet of marble valued at \$107,400, was produced.

The marble in the Columbia district occurs as irregularly shaped masses of dolomite in metamorphosed limestones of the Calaveras group of Paleozoic age. The limestones are exposed in a belt, approximately 25 miles long and 1 to 5 miles wide, trending roughly northwest. The bedding is generally indistinct and steeply dipping. The marble is a dense, fine-grained dolomite that takes a fine polish. The stone weighs 169 to 182 pounds per cubic foot and has a compressive strength of 25,000 pounds per square inch. The stone most commonly quarried is white with blue veining. A buff stone with reddish veining also was produced.

Four quarries were active between Columbia and Sonora. The largest of these were the Columbia Marble Quarry which operated from 1891 to 1942 and the Bell Columbia Marble quarry which operated from 1918 to 1926. At the original Columbia Marble quarry, a marble mass 150 feet wide was exposed for a depth of 800 feet. A later pit opened in 1921 revealed a marble mass 200 feet wide, 500 feet deep and a mile long. Quarrying was done by channeling machines which cut three sides of 16 x 12 foot blocks. The blocks were then drilled horizontally, broken out by the plug-and-feather method, and hoisted to the eight gangsaws located above the quarry. The cut slabs were polished, and shipped to San Francisco for interior use as flooring, steps, and wainscoting. The only recent production from this district has been crushed stone for terrazzo and chemical use (see crushed stone and limestone sections for more thorough discussions of these operations).

From 1896 to 1950, several localities in San Bernardino County yielded 185,388 cubic feet of dimension

stone marble valued at \$343,076. The main periods of activity were from 1902 to 1909 and 1936 to 1941. The bulk of the early production came from Slover Mountain, near Colton, where a recrystallized limestone of probable Paleozoic age occurs as roof pendants in granitic rocks. The poorly defined limestone strata which strike N. 70° E. and dip 45° east, are more than 2,000 feet thick. The dimension stone quarries, which were on the south side of the mountain, were leased from the California Portland Cement Company which also worked the deposit for cement and continues to do so (see sections on cement and limestone in this volume). The stone ranges from a coarsely crystalline, white variety to a finer-grained blue-gray variety, and contains disseminated flakes of graphite. It is dense and takes a good polish. Beds 5 to 7 feet thick were worked in the quarries and were broken by hand drilling and by blasting with black powder. Blocks were cut and polished and were marketed as interior venter in San Francisco and Los Angeles. The dimension stone quarries were shut down by 1910.

The Vaughan Marble quarry, 5 miles north of Cadiz in San Bernardino County, was active from 1937 to 1939. The quarry is in marble beds that crop out in a northwest-trending belt of Cambrian sedimentary rocks that contains quartzite, shale and limestone, and is about 2 miles long and 1 mile wide. The marble beds average 20 feet in thickness and dip 35 to 55 degrees. Blocks of black and blue-black variegated colors weighing 15 to 20 tons were removed from two small quarries and shipped to Los Angeles for cutting and polishing.

In 1915 and 1918, small tonnages of marble were produced from the Three Colored Marble quarry on the northeast slope of Sidewinder Mountain also in San Bernardino County. The deposit is a multi-colored sedimentary breccia about 200 feet thick, consisting of white irregular dolomite fragments in a green and black matrix of dolomitic limestone. The fragments were derived largely from the underlying Carboniferous Oro Grande series. An open cut, 20 feet wide, 30 feet high, driven 20 feet into the hill is the only working. In the quarry, east-striking and steeply dipping joints limited the size of blocks obtained. Blocks as much as 9 feet in longest dimension were removed by blasting, and rolled downhill where they were loaded by block and tackle onto wagons and trucks and shipped elsewhere for cutting and polishing (Bowen, 1954, pp. 146-148). The stone was used for ornamental purposes.

Verde antique marble was produced intermittently from 1890 until the early 1900's at the Verde Antique Marble quarry 15 miles northeast of Victorville. The rock is a serpentinized marble derived by contact metamorphism of a roof pendant of dolomite of the late Paleozoic Oro Grande series. The marble is colored variously in combinations of yellow, chocolate, black, blue, red, gray, cream, rose, and white. The predominant colors are yellow, white and brown. The bands of serpentinized marble strike northwest, dip southwest and range from 3 to 6 feet in width. The chief working is a level quarry near the top of an 1100 foot mountain. The quarry is 60 to 100 feet wide, 75 feet high and extends 50 feet into the hill. Blocks were blasted and dragged to the base of the hill, loaded onto wagons and taken to Victorville. The stone was shipped by rail to Colton where it was sawed and polished and sold for use as interior decorations in



buildings in Los Angeles and San Francisco (Aubury, 1906, p. 147, and Bowen, 1954, p. 148).

Marble dimension stone was first produced in Inyo County in 1888 when the Inyo Marble Company began quarrying operations low on the west flank of the Inyo Mountains between Keeler and Lone Pine. Production in Inyo County was reported during the periods 1894-1898, 1903-1907, and 1913-1914, when 78,400 cubic feet of dimension stone marble valued at \$219,300 was produced. The entire output is believed to have come from the property of the Inyo Marble Company (Logan, 1947, p. 244).

Paleozoic sedimentary rocks containing abundant limestone and dolomite are discontinuously exposed for many miles along the east margin of Owens Valley. Quarrying operations have been confined to Silurian and Devonian dolomite which underlie a belt half a mile wide, 6 miles long, and are at least 500 feet in exposed thickness. The beds dip northeastward at a high angle and are highly fractured. Three varieties of fine-grained, dense dolomite were quarried—white, yellow, and variegated white with black manganese dendrites. During the early years of production, rough marble blocks weighing 15 to 18 tons each were removed and shipped by rail to Truckee where the company had a sawing and polishing plant. This marble was used in many buildings in San Francisco. Since 1915, the property has been worked as crushed stone for chemical use, and in the manufacture of roofing granules and terrazzo chips (see sections on crushed stone and limestone).

Marble also has been produced in small quantities in Amador County near Plymouth and at Crestmore in Riverside County. In the 1890's some "onyx marble," aragonite, was quarried from a deposit 17 miles northeast of Arroyo Grande in San Luis Obispo County.

#### Slate

Slate is a fine-grained rock produced by the regional metamorphism of clay or shale. Pressure and heat cause the shaly material to partly recrystallize to platy, micaceous minerals in parallel orientation. The cleavage thus produced is sufficiently well-developed to allow easy splitting of the rock and is the feature of greatest economic importance. The predominant minerals in mica slate are muscovite, quartz, chlorite, and carbonaceous matter.

The commercial value of slate depends upon mineralogical composition, structure and texture. Permanence of color is especially desirable. Some slates maintain their original color for many years, whereas other slates change shades within a comparatively short time. Color is determined by chemical and mineralogical composition. Gray, blue-gray or black color is attributed to the presence of carbonaceous material; green if chlorite is abundant; red, purple, yellow or brown have oxides of iron. Some color changes are attributable to the decomposition of carbonates of iron, calcium or magnesium to form the yellow hydrous iron oxide, limonite.

The cleavage generally must permit the slate to split along smooth planar surfaces. A second direction of splitting, "the grain," is approximately at right angles to the slaty cleavage and is also of economic importance. Some of the slates that have rough uneven surface and are vari-colored are desired for their decorative qualities.

The most undesirable impurity in slate is calcium which generally is present as the carbonate. Sulfur fumes acting on calcium carbonate form calcium sulfate (gypsum) which expands during crystallization and causes the slate to split or crack. Iron sulfides oxidize to form spots and stains. Nodules of silica are present in some slates and cause difficulty in working. The principal uses of dimension slate are for roofing, blackboards, school slates, electrical panels and structural products. Slate also is crushed to produce roofing granules as described in the crushed stone section of this volume. Slates suitable for blackboards and bulletin boards must be soft and of uniform color and texture. For structural products, such as floor tile, hearths, flagging, and window sills, the slate should be soft, even-grained and preferably not highly fissile. Electrical slate should be low in magnetite, carbon and other low-resistance minerals, and able to be cut and drilled without scaling (Bowles, 1939, p. 236).

Approximately \$700,000 worth of slate dimension stone has been produced in California (Averill et al., 1948, p. 92), since it was first produced in 1889. Peak years were in 1903 and 1906 when approximately one million square feet a year were produced. The output held firm through 1910, but since has been erratic.

Most of the slate production in California has been obtained from the Jurassic Mariposa formation which is exposed in the western foothill belt of the Sierra Nevada in Mariposa, Tuolumne, Calaveras, Amador, El Dorado, and Placer Counties. The Mariposa formation originally consisted of shales with minor amounts of interbedded sandstones and conglomerate. Near the close of the Jurassic period, the formation was folded and locally intruded by granitic rocks, and the shaly material recrystallized into slates and phyllites. The productive slate quarries in California are in a slate-bearing belt that trends northwest from Calaveras to El Dorado County for approximately 65 miles, and ranges from 1 to 3 miles in width. The schistosity strikes northwestward and dips steeply to the northeast, irrespective of the attitude of the original bedding.

The Placerville district in El Dorado County was the most extensively and continuously worked source of slate in the state. Mining of slate at this locality began in 1891 or earlier (Aubury, 1906, p. 150). Seven quarries operated between the settlements of Placerville and Kelsey. The most productive was that of the Eureka Slate Company whose quarry extended to both sides of a small canyon where the slate is a blue-black color and weathers brown to greenish-gray. The quarry face was 200 feet long and 70 to 200 feet high. Blocks were loosened by drilling and wedging and removed by cable-boists. They were then split by hand into roofing slabs. The oldest quarry in the district, the Chili Bar Mine, operated until 1897. In 1928, the Pacific Minerals Company installed a mill on this property and has been producing roofing granules and dust filler until the present time (1956). This operation and roofing granules in general are discussed in the section on crushed stone.

In Placer, Calaveras, Tuolumne and El Dorado and Mariposa Counties, slate for building veneer and flagging was produced sporadically from 1937 to 1940 and from 1945 to 1946. Of these operations, the only one that was active in 1956, was a small quarry, the Agua Fria,





FIGURE 8. Agua Fria slate quarry near Mariposa, Mariposa County. Slate flagging is stockpiled in the foreground. The slates split along the plane of schistosity.

in Mariposa County. Here two men, using hand quarrying methods, were intermittently removing a small tonnage of slate suitable for use as flagging.

#### Basalt and Related Rock Types

In commercial usage and in the discussion to follow the term "basalt" is applied to any of the dense, fine-grained, dark-gray or black volcanic rocks including some that geologists refer to under the more specific names of dacite, andesite, latite, and trachyte as well as basalt in the strict sense. All of them have similar physical properties. The light-colored volcanic rocks are discussed below with the miscellaneous group.

Basalts suitable for dimension stone are hard, tough, even grained and dense. They generally have a well defined rift and grain and can be split easily without fracturing into large blocks. Basalt is most valued for its ability to resist shock and abrasion, a property that led to an early and extensive use of basalt for paving block. Basalt paving blocks are still preferred in certain industrial and warehouse areas subject to heavy traffic. They also are used locally between streetcar tracks, because they can be taken out and easily replaced during repair work. The predominant use of basalt is as crushed stone (see crushed stone section).

In California, basalt has been quarried for both paving block and building stone, and an estimated 3 million dollars worth of basalt paving block has been produced (Averill et al., 1948, p. 98). Basalts and related rocks are extensively exposed in many localities in the state. Tertiary and Quaternary basaltic rocks are exposed for hundreds of square miles in the Modoc Plateau in the Sierra Nevada, Mojave Desert, Coast Ranges and Peninsular Ranges provinces (see crushed stone section).

Past production of basalt centered about a score of operations in the counties immediately north of San Francisco—Marin, Sonoma, Napa, and Solano. Most of these lie near the settlements of Napa, Petaluma, Cordelia, Novato, Kenwood, Santa Rosa, Sonoma and St. Helena. The basalts occur as interbedded flows in the

Pliocene Sonoma volcanics which are exposed over a 350 square mile area.

The periods of peak production years were 1887 to 1891 and 1906 to 1913. More than 50 individual quarries were active from 1864 to 1913. Many of the quarries were located so that the cut block could be barged to the San Francisco Bay area. The quarries were small and ordinarily employed only a few men. Sonoma County, the principal source, supplied the most blocks for the streets in the cities of the state. The demand for smoother pavement caused a slump in the paving block business, and by 1913 virtually all the quarries were inactive. Many of the quarries were subsequently reactivated to produce crushed rock and some are still active in that capacity (see crushed stone section).

#### Miscellaneous Stone

Embraced in the general designation of "miscellaneous stone" is a wide variety of rocks, other than those already discussed, that commonly are attractive enough to be used as dimension stone. These include light-colored volcanic rocks, mica schist, and siliceous limy shale. The important characteristics of these rocks are color, natural appearance, durability and workability. The colors ordinarily are pleasing shades of off-white, yellow, cream, buff, and pink. The stone should be easily quarried, soft enough to split by hand or by a block-splitting machine, yet durable enough to withstand weathering. Most of the rocks in this group occur as layered rocks with natural partings along bedding planes or along planes of schistosity.

Many of the light-colored volcanic rocks have buff, red, and purple bands or pseudo-concentric patterns which have an eye-catching appearance. In general they are comparatively soft, and are easily quarried and sawed or split.

The mica schists ordinarily split along the planes of schistosity and show shiny lustrous surfaces produced by the dimensional alignment of the micaceous minerals. Such surfaces commonly are stained by iron-oxides which give the stone a rustic, weathered appearance.

At many places in California siliceous limy shales crop out in gently dipping, thin beds that split readily along the bedding plane and hence can be easily quarried. This stone can be worked by hand or by block splitting machines. The calcareous types are uniform in texture and color, in shades of light brown, gray and cream. The more siliceous types are thinly laminated and split crudely to present a rough exterior surface.

Quartzites used for dimension stone differ radically from the stones previously described. Quartzite is a hard, tough, dense rock that is difficult to quarry, requiring blasting. The stone is ordinarily shaped entirely by hand as there is generally only one parting surface, a joint plane. However, the stone has a pleasant non-uniform appearance because of pale red and pink iron oxide stains on the quartz grains.

In California, the principal uses of these miscellaneous stones are as building stone (ashlar, rough block, and rubble) and as flagging. The Pelona mica-schist in Los Angeles County, and Monterey siliceous shale near Carmel in Monterey County were quarried as early as 1927. These and other operations were active intermittently on a minor scale until about 1950, when the building boom



created a new demand for stone. By 1955, the value of the annual production of miscellaneous dimension stone in California had increased to approximately \$440,000. The bulk of production has been from the sedimentary rocks of the Monterey formation and from the Pelona schist.

*Monterey "Shale."* Fine-grained siliceous limy sediments of the Miocene Monterey formation crop out in the southern Coast Ranges, the Transverse Ranges, and the Peninsular Ranges. The rocks are thinly bedded, dip at low angles in many places, and range from off-gray to buff-brown in color. In 1955, dimension stone valued at over \$375,000 was produced from this formation.

In 1956, the most productive building stone operation in California was at the site of a former diatomaceous earth operation of the Great Lakes Carbon Corporation in the Palos Verdes Hills of Los Angeles. The Palos Verdes Stone Division of this company has directed activities on their 1000-acre holdings since 1953 when the building stone production began. The stone is a hard, siliceous, stratified mudstone, pale-gray to nearly white in color, that splits easily along the bedding plane. The strata, which dip gently and crop out on the crests of low rolling hills, are bulldozed to depths of 4 feet and piled in windrows. Laborers using sledges split the larger boulders into irregular blocks approximately 3 x 4 x 6 inches. No splitting machines are used. About 100 tons of stone each day is hauled from the field into a quarry yard where it is picked up by the purchasers. The stone, called "Palos Verde Stone," is marketed solely as rubble and is used extensively throughout California for walls, building fronts, fireplaces, swimming pools and patios. Shipments also have been made to the eastern states.

In Tepesquet Canyon east of Santa Maria in Santa Barbara County, a light-buff to cream, thinly bedded limy siltstone member of the Monterey formation has been quarried since 1939. The beds dip at about 35° in this quarry and six separate layers are worked. Fork

lifts and crowbars are used to wedge out the slabs of stone. The slabs are trucked to the floor of the quarry where they are first trimmed by hand, split by two guillotine-type machines, and stacked on pallets. This rock is quarried by G. Antolini and Sons of Santa Barbara and is sold under the trade name of "Santa Maria Stone." It is marketed throughout California by authorized stone dealers. The capacity of the operation is about 400 tons a month of cut block. The stone is used as ashlar for interior and exterior building purposes.

A buff-colored siliceous shaly limestone has been quarried since 1927 near Carmel in Monterey County by A. L. Passadori. Four thin layers, 6 to 12 inches thick, are worked and four types of rock produced for use as flagging, rough block, ashlar and rubble. (Galliher, 1932, pp. 15-41). The quarry is worked entirely by hand and no cutting machine is used. Only a small tonnage of stone was being produced in 1956. The stone has been used extensively in the Monterey Bay area to veneer small homes.

*Pelona Schist.* A dark-gray, iron-oxide stained quartz-mica schist of the pre-Cambrian (?) Pelona schist series has been quarried since 1927 at several localities north of Saugus, Los Angeles County. The schistosity plane is the only plane of fracturing and ranges in dip from 15° to 20° at Del Sur Ridge, 45° to 50° in Bouquet Canyon, and 70° to 80° in San Francisco Canyon. Blasting and bulldozing expose suitable faces and slabs, and blocks are broken out and split by hand with crowbars, hammers, and chisels. In the largest quarry, located on the top of Del Sur Ridge between Bouquet and San Francisco Canyons, a bulldozer and a steam shovel are used to break up the schist. In 1956 approximately 200 tons a month were being produced from all the quarries in the schist. These are marketed under the name "Bouquet Stone" and are used throughout California for interior and exterior building veneer and as flagging (Gay and Hoffman, 1954, p. 533).



FIGURE 9. "Palos Verde stone" operation in Palos Verdes Hills, Los Angeles County. Siliceous mudstone of the Monterey formation is ripped up by a bulldozer to a depth of 4 feet and split to size with sledges.



FIGURE 10. "Santa Maria stone" quarry near Sisquoc in Tepesquet Canyon, Santa Barbara County. Six different beds of calcareous siltstones of the Monterey formation are quarried and split into building block.



*Light-Colored Volcanic Rocks.* Rhyolite tuff of the Miocene Valley Springs formation has been quarried in the foothills of the Sierra Nevada, since the early 1850's. This light-colored rock was quarried for buildings in the Mother Lode from Dutch Flat to Angels after disastrous fires destroyed many gold-mining towns (Heizer and Fenenga, 1948, pp. 91-164). The earliest quarrying was centered about Mokelumne Hill in Calaveras County. The Peirano Quarry at Altaville, Calaveras County, is still active, but is worked only for roofing granules.

A buff-colored rhyolite tuff has been quarried at several localities near Placerville, El Dorado County, since 1948. The rock, a massive vitric crystal rhyolite tuff, in places as thick as 400 feet, is extensively exposed in this area. It is colored light-gray to buff by various amounts of limonite commonly in pseudo-concentric patterns. The principal operation is the Sierra Placerite quarry which is 100 feet long, 50 feet wide and 15 feet high. The rock is drilled and blasted and hauled to a plant nearby for cutting. The pieces are sawed on circular tungsten carbide saws and then split with a hydraulic cutting machine. Some of the sawed stone is fired in kilns to heighten a color effect. The buff colors change to various shades of pink and red. Both stones are sold fired and unfired under the name "Sierra Placerite." The capacity of this operation is an estimated 100 tons of stone a month. "Sierra Placerite" is used predominantly in the San Francisco Bay area as ashlar in interior and exterior building fronts and fireplaces (Clark, 1956).

Banded, light-gray and purple flow rocks of the Tertiary Sonoma volcanics have been quarried at several localities near Glen Ellen in Sonoma County since 1928. The rock is a banded riebeckite rhyolite that splits readily along well-defined and closely spaced parting planes which are usually stained with brown limonite. The layers are generally nearly horizontal and are worked by benching. The stone is split by hand for flagging and in some quarries splitting machines are used to obtain blocks. The so-called "Sonoma Stone" has been used throughout California as ashlar and flagging. Four quarries were active in mid-1956, but on a small scale.

*Quartzite.* A red, iron-oxide stained quartzite is being quarried, in small tonnages, at Suncrest, San Diego County. The rock, massive with steeply dipping joint planes, occurs in a pendant of pre-Cretaceous metamorphic rock in granitic rock. Blocks are blasted with dynamite, pried loose, and split with plugs and feathers. The stone is sold as rubble for facing in the San Diego area, and is named "Red Rose Quartzite." Three men are employed at the quarry.

*Field stone or Garden Rock.* Every stone yard in California has stock piles of materials often termed "garden rock," which have been obtained locally. These are known as "field stones" and consist of rock that is picked up off the ground without any quarrying or other treatment. These rocks do not technically classify as dimension stone, although they are used for many building purposes. The amount of field stone sold in California is difficult to estimate. Among the many rocks thus used are moss-covered boulders of basalts, deeply weathered silica-carbonate rock, glaucophane schist, "burnt" shale, mariposite, limestone, lichen-covered serpentine, and wollastonite.

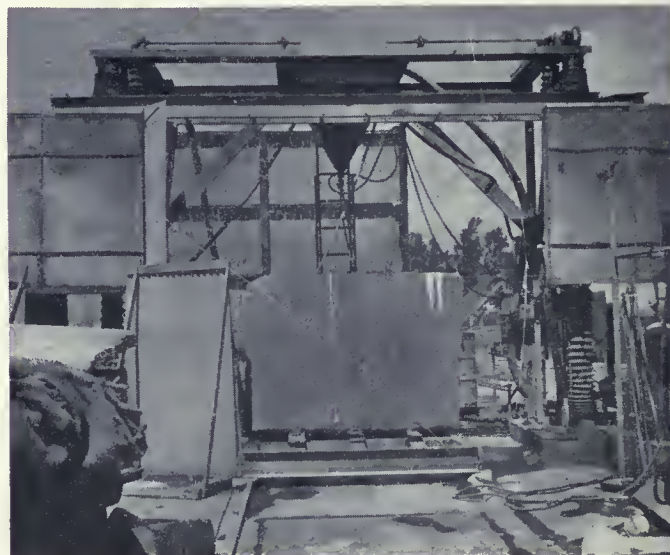


FIGURE 11. Single strand, high carbon steel wire saw starting to cut a block of granite. Carborundum used as abrasive is fed with water through a funnel. Cutting rate is from 6 inches to 12 inches an hour.

One of the more productive field stone operations in California is on the southwest slope of the Big Maria Mountains about 20 miles north of Blythe, Riverside County. Here, erosional fragments of gray and dark brown wollastonite, a calcium silicate mineral, have been gathered by the Melvin L. Jontz Company of Los Angeles. The wollastonite occurs as fine-grained bodies in crystalline limestone of the Maria formation of probably Paleozoic age. The loose, weathered pieces of rock are picked up in the field, loaded on a sled-like "boat" attached to a cable and dragged to a truck for loading. The wollastonite is marketed under the name "Driftwood" and is used as ornamental garden rock and for building exterior and interior walls and fireplaces. Al-

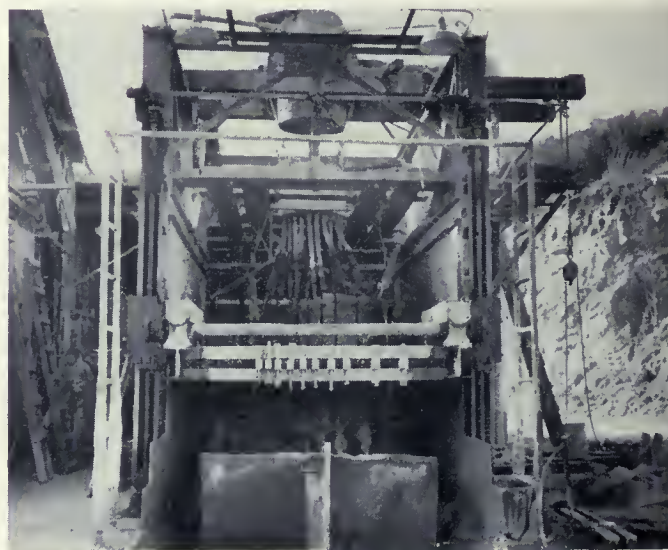


FIGURE 12. Gang saw cutting block of "black granite." Steel shot used as abrasive is fed with water through hoses to the soft steel cutting blades. The width and number of cuts can be varied. Cutting rate is about 1½ inches an hour in this type of granite.



though sold principally in the Los Angeles area, this rock has been shipped as far north as Seattle, Washington, and as far east as Milwaukee, Wisconsin. The capacity of this operation is about 400 tons a month.

#### QUARRY METHODS

Quarrying practices vary in accordance with the degree of induration of the rock, presence of directions of easy splitting and the manner in which the rock crops out. The harder rock types such as granite must be drilled and blasted. Granite is quarried from massive exposures by drilling with pneumatic drills attached to hollow drill steel and detachable tungsten carbide bits and by blasting with small charges of black powder along the grain and the run. The stone is split along the rift by drilling shallow holes and driving wedges or "plugs and feathers" in the holes. "Feathers" are strips of iron that are flat on one side and curved on the other. Two feathers are inserted, flat sides together, in a drill hole and the plug, which is a steel wedge about 6" long, is driven between them. The plugs are then sledged lightly in succession until a fracture appears.

In some deep quarries the granite is channeled by drilling closely spaced rows of holes and broaching or cutting out the narrow webs or cores between them. This method is used in preference to blasting because, although slower and more costly, it gives a straight surface and does not cause shattering. It is most advantageous for making cuts in the plane of the "hard way."

Granite boulders are worked either in the quarry face or rolled to the quarry floor. The boulders are split by drilling a hole to the center and blasting with a light charge of black powder. The blocks are then split by wedges, plugs and feathers.

The large quarried blocks are cut by wire or gang saws. Wire saws are endless belts of 1- to 3-stranded high carbon steel cable that are used to make secondary cuts but in one quarry will be used to make primary cuts. The wire, fed by a mixture of carborundum and water, cuts by abrasion. Single strand wire is  $\frac{3}{16}$ " in diameter and is twisted every 50 feet in a reverse direction. A small wire saw can cut a 3- by 5-foot block of granite at the rate of 10 to 12 inches an hour, after which the wire must be replaced. Most wire saws make only one cut at a time, although the Escondido Granite Company, Escondido, in early 1956, was using a saw that had four wires and made four simultaneous cuts at a reported rate of 1 foot an hour.

A gang saw is composed of a number of soft steel blades  $\frac{1}{2}$  to  $\frac{5}{8}$  inches thick set in a frame. The blades are notched about a foot apart in the lower edge to carry steel-shot abrasive beneath them. Blocks of any width may be obtained by adjusting the spaces between the blades. The rate of cutting is about 3 inches an hour.

Further cutting of the block is done by circular diamond saws. The surface of the cut stone is finished by using a horizontal circular wheel, first by grinding with silicon carbide, followed by polishing with aluminum oxide, and buffing with putty powder (tin oxide) (see fig. 14). Lettering on memorial stones is now done almost exclusively by sandblast technique although hand carving is still practiced. Previous to sand blasting, the polished stone is covered by a thin template made of a rubberized compound or paper masking tape on which



FIGURE 13. Block of "black granite" that has been cut with a gang saw.

the letters have been outlined. The stone is then placed in a closed chamber and a stream of powdered carborundum under pressures of 80-100 psi., is directed against the design for a few minutes. The exposed hard granite is quickly cut away while the abrasive has little or no effect on the template.

Softer rock types such as marble and sandstone are quarried by drilling and blasting or by the use of channel machines. These machines make primary cuts, approximately 4 feet apart, by means of the chopping action of 3 to 5 steel bars. Channel machines are more adaptable to essentially level quarries as they are mounted on frames that travel on tracks. After the channeling cuts are made, blocks are wedged loose with plug and feather or cut with wire saws. Slate is loosened



FIGURE 14. Machine used to grind and polish granite. Rough blocks are imbedded in plaster of paris. As the horizontal head revolves, it is moved back and forth over the blocks. The first grinding is done with carborundum, polishing with aluminum oxide, and buffing with tin oxide.





FIGURE 15. Map showing principal sources of dimension stone in California.



by hand with pry bars and sledges, by drilling and wedging, or by the use of wire saws.

The thinly bedded miscellaneous types such as schists, layered volcanic rocks, siliceous shales are removed by using pry bars or fork-lift trucks after small charges of black powder have loosened the rock. These stones are further split by hand, circular saw or block-splitting machine. This machine is a mechanically operated guillotine-type cutter which operates under hydraulic pressure.

#### MARKETS AND PRICES

As stone is a heavy product, weighing 160 to 170 pounds per cubic foot, transportation expense commonly constitutes a very large fraction of the delivered cost. Typical railroad rates for crude granite block are as follows: Daulton (the nearest railhead to Raymond) to San Francisco—\$130 per 30 ton carload; Daulton to Los Angeles—\$204 per 30 ton carload; Daulton to Sacramento—\$119 per 30 ton carload; Escondido to Los Angeles—\$84 per 20 ton carload; Escondido to San Francisco—\$176 per 20 ton carload. Typical truck rates are as follows: Raymond to nearest railhead (21 miles)—\$32 per 18 ton carload; Raymond to San Francisco—\$106 per 18 ton carload; Raymond to Sacramento—\$92 per 18 ton carload. Nevertheless, California dimension stone is shipped long distances to satisfy demand for certain textures and colors. Two-thirds of the monumental stone produced in California is shipped out of state, much of it on an exchange basis for eastern stone. Monuments are trucked to Washington and Oregon and shipped by rail as far as Texas and Minnesota.

The crude blocks of dimension stone that are quarried for monuments are sold to finishing plants or are partly finished by the quarry owners who sell either to other finishing yards or directly to the small local stone yards. The monumental stone market is virtually limited to stone from specific localities that has become widely known and used. Therefore, it is difficult if not impossible to open a monumental stone quarry and put a new stone on the market. Even the reopening of a quarry that has been idle for just a few years is very difficult.

In 1955, the value of rough granite block for use as monumental stone in California was \$4.25 per cubic foot f.o.b. the quarry in California. Dressed monumental stone was valued at \$8.50 per cubic foot. The market for building stone depends primarily upon the desires of architects and builders who recommend or specify certain types of stone for specific jobs. The popular demand is for special types of pink, red, or black granite and yellow, red, veined or brecciated marble that are not produced in California. Granites are shipped in from Georgia, Vermont and Minnesota along with those imported from Finland, Sweden and Canada. Marbles are imported from Italy, Spain, France, Belgium, Portugal, and England. Onyx marble is imported from Mexico. Cut slabs of Tennessee and Vermont marble are shipped in by rail to be finished by company-owned plants in California.

The imported marbles and granites are finished and sold by plants in the Los Angeles and San Francisco areas that primarily fabricate marble. The California granite that is used as facing on buildings is obtained

from the same quarries and finishing plants that supply block for monumental stone.

Crude blocks of imported dimension stone, some used as ship ballast, reach American ports as cheaply as stone quarried in the United States. The import duty which was levied in 1950, is 10¢ (formerly 25¢) per cubic foot on rough granite blocks and 32½¢ (formerly 65¢) on rough marble block. Imported block sells for from \$5 to \$20 per cubic foot f.o.b. San Francisco.

Since 1950, natural stone facing has been used increasingly in homes and small commercial buildings in California. This is particularly true in southern California where competition has swung contractors to the use of stone as a selling feature. Red and buff colored sandstone shipped in from Arizona was the predominant building stone used as facing in California until 1950. Arizona stone is gradually being replaced by native California stone which is not as uniform in texture or as neat appearing. This is because of public demand for rock types that give a rustic or natural appearance. In northern California, more stone is gradually being used, particularly in new developments such as the shopping centers at Stonestown in San Francisco, and Hillsdale in San Mateo. The proportion of California stone to Arizona stone has risen in northern California from 10 percent to 30 percent. In southern California about equal proportions of Arizona and native stone are being used (1956).

A factor of great importance in the promotion of stone for veneer is the difficulty with which the stone can be laid up. Crude stone with its irregular shape and only one smooth surface, is hard for the ordinary brickmason to lay. In southern California stonemasons have become accustomed to working stone and, in fact, may prefer stone to brick. In the rest of the state many brickmasons are reluctant to attempt a job with stone.

Informal building stone (ashlar, rubble and rough block) is sold to wholesale stone dealers, or at the quarry to owners of local stone yards and building contractors. The price of this type of stone ranges from \$22 to \$28 a ton f.o.b. the quarry. An estimated 3,000 tons a month of informal building stone are used in California.

The problem of assuring a steady supply of the same quality stone faces all building stone producers. An architect or building contractor hesitates to contract the use of a stone where there is any question of change in color, texture, or hardness in future shipments of the stone. Many small quarries are opened in acceptable stone and yet are not successful because delivery of specific tonnages cannot be assured. This means that, in order to sell a new stone to an architect, enough material must be quarried and stockpiled beforehand, making this type of venture essentially a gamble in capital investment. Developing a marble building stone deposit in California would depend upon many factors, especially the (1) acceptance by local architects in preference to such well-known stones such as Italian and Vermont marble, and (2) the delivery of blocks at a price competitive with foreign or eastern imports. Aside from transportation, the biggest cost item and the most decisive is the labor cost of quarrying. In 1956 the prevailing wage scale for a stone worker was \$23.80 a day. The necessities efficient large-scale quarrying and use of the most modern labor-saving equipment. A moderate-scale operation probably





FIGURE 16.

would require an initial expenditure of approximately \$100,000.

The outlook for expansion of the dimension stone industries is fair. The market for monumental stone has been growing and the merits of using natural building stone are being increasingly recognized by architects, builders and the general public. The new use for granite as surface plates will help production a little.

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## STRONTIUM MINERALS

By WILLIAM E. VER PLANCK

Although California's strontium reserves are among the largest in the United States, distance from the principal markets, which are in the eastern United States, and comparatively low grade generally have made them uneconomical to mine in normal times. Strontium minerals were mined in California from 1916-18 and again from 1939-46 when imports were restricted and the demand was unusually great. Beginning in 1952, small quantities were again being produced for local use. All of the strontium minerals produced in California have come from three localities: the Fish Creek Mountains deposit in San Diego County; deposits on the south slope of the Cady Mountains, San Bernardino County; and deposits in the Mud (Strontianite) Hills 10 miles northeast of Barstow. Additional reserves exist in the northern foothills of the Avawatz Mountains and in Bristol Lake, San Bernardino County.

Deposits of strontium minerals occur also in Arizona, Ohio, Texas, Utah, and Washington. Imports to the United States, which are in the range of 5,000 to 10,000 tons per year, have come principally from England and Mexico in recent years.

**Mineralogy and Geologic Occurrence.** Celestite ( $\text{SrSO}_4$ ) and strontianite ( $\text{SrCO}_3$ ) are the only strontium-bearing minerals that have been mined in California. Celestite, which is much the more common, forms concretions and beds in sedimentary rocks. The deposits in California are associated with gypsum or lake sediments, but in other areas celestite is found also in other types of rock, especially limestone. Much more rarely celestite occurs in hydrothermal veins. Deposits of strontianite are rare, not only in California but throughout the world. In California, strontianite deposits of possible commercial value occur as nodules and concretions in shaly tuff.

**Strontium Resources.** Most of the strontium minerals mined in the United States have come from Texas. Celestite occurs in two localities: near Brownwood, Brown County, and near Sweetwater, Nolan County. In both localities the celestite is a replacement of carbonate rocks. Reserves, most of which are in Brown County, have been estimated to be 271,000 tons of celestite rock of an average grade of 73 percent  $\text{SrSO}_4$  (Fine and O'Meara, 1944).

The largest source of the strontium minerals used in the United States is near Yate, Gloucestershire, Great Britain. The total production from this area is about 400,000 tons. Celestite occurs as irregular masses and lenticular bodies associated with the Triassic Keuper marl. The celestite bodies are located by probing with a boring tool and mined by excavating pits up to 20 feet square and 15 to 20 feet deep (Harness, 1942, pp. 3, 4). The celestite is then washed, broken into lumps, and shipped. Typical material shipped contains more than 95 percent  $\text{SrSO}_4$ .

Since about 1943, a significant portion of the celestite used in the United States has come from Mexico. During World War II, E. I. du Pont de Nemours & Company obtained some high-grade celestite from near Bermejillo,

Durango, where narrow celestite veins occur in limestone. The du Pont Company owns celestite deposits at El Tule, northern Coahuila, where celestite associated with fluorspar forms veins 6 feet or more thick in limestone. Selected samples that are free from gangue contain more than 98 percent  $\text{SrSO}_4$ . Because of high transportation costs, production has been negligible. It is believed, however, that if for any reason the existing sources should not be able to satisfy the United States' demand for strontium minerals, the El Tule deposits would be opened and could produce as much as 20,000 tons per year of celestite for at least 2 to 3 years (Gillson, J. L., 1955, personal communication).

**Localities in California.** By far the largest reserves of strontium minerals in California occur in the foothills of the Cady Mountains about 8 miles northwest of Ludlow, San Bernardino County. Here celestite beds crop out discontinuously along a west-trending belt that is about 6300 feet long. The celestite is interlayered with thin-bedded tuffs and clays that are overlain by limestone and underlain by a thick series of volcanic rocks. All of these rocks are Tertiary in age.

From 10 to 30 percent of the tuffs and clays have been replaced by chalcedony. Most of the celestite is in the form of beds up to 2 feet thick, but some of it occurs as beds of concretions in sandy tuff or clay. Celestite beds up to an inch thick, and separated by impure material, form celestite-rich units as much as 10 to 12 feet thick. A maximum of 112 feet of celestite occurs in a section 410 feet thick. The celestite is a finely crystalline, light-colored buff to greenish rock, most of which contains 5 to 10 percent of silica and lime. Estimates of the reserves vary widely. Durrell (1953, p. 47) placed them at  $1\frac{1}{2}$  to  $2\frac{1}{2}$  million tons of celestite of 81 percent grade to a depth of 50 feet. J. A. Stephens of the Excel-Mineral Company, present owner of the property, believes that only 100,000 to 200,000 tons of celestite could be profitably recovered (personal communication, 1955).

The Fish Creek Mountains deposit, San Diego County, is on an outlying hill north of the gypsum deposit of the United States Gypsum Company and less than half a mile west of the Imperial County boundary. Celestite forms a cap up to 8 feet thick on this hill. The celestite is underlain by gypsum which in turn rests upon gray conglomerate of the Miocene Split Mountain formation. The celestite is underlain in some places by a breccia 2 to 5 feet thick composed of angular blocks of gypsum and celestite. A representative sample from this deposit contained 93.8 percent  $\text{SrSO}_4$ . Reserves have been estimated to be more than 10,000 tons (Moore, 1935, p. 369), but several thousand tons were mined during World War II.

In the northern foothills of the Avawatz Mountains, San Bernardino County, celestite occurs in the salt- and gypsum-bearing Tertiary lake beds that are described in the section on gypsum in this volume. The celestite is found mainly in the gypsiferous member and is most abundant in the western part of the area. The celestite occurs as small nodules in gypsum, spheroidal conere-



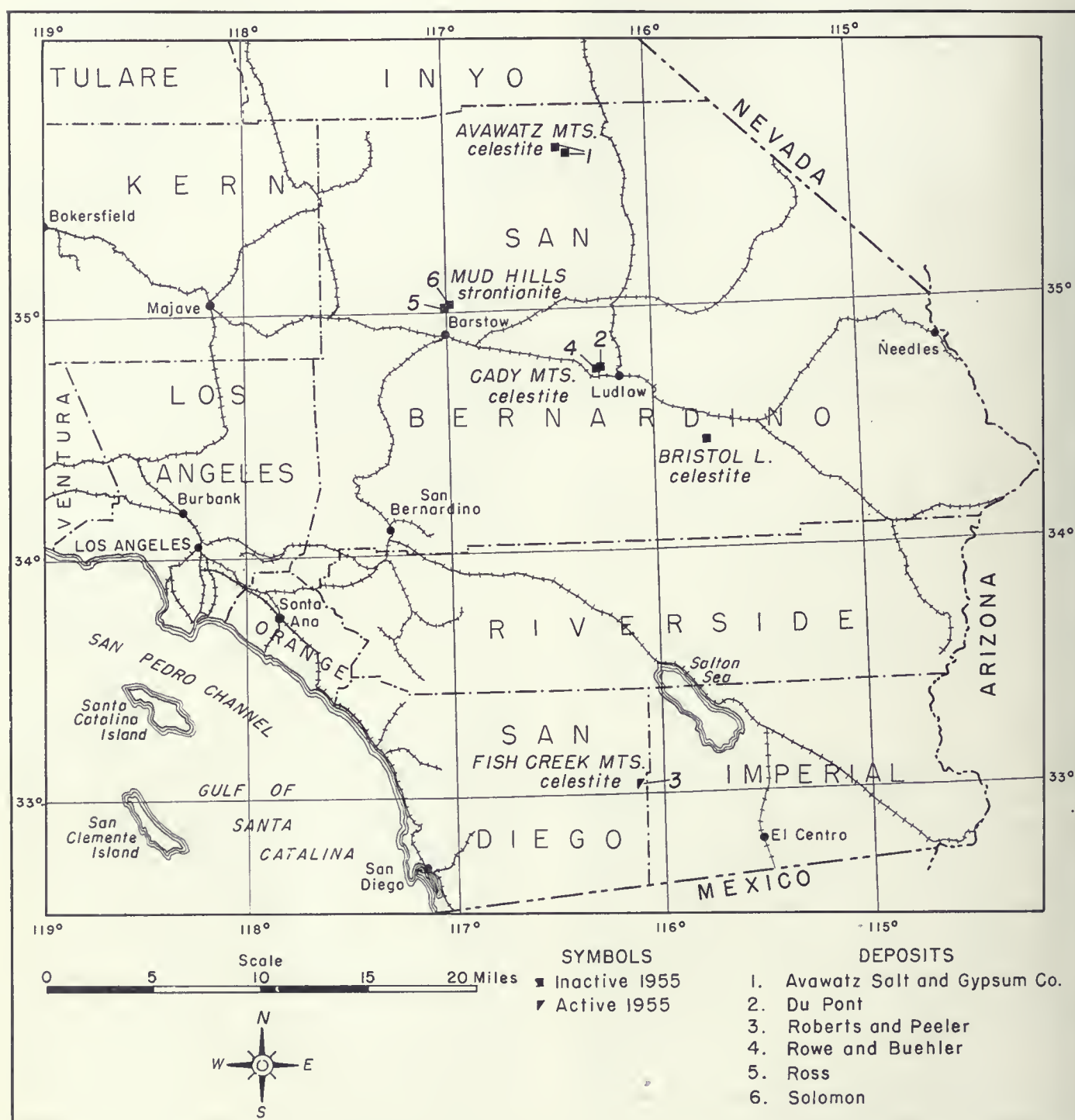


FIGURE 1. Map of a section of southern California showing location of strontium deposits.



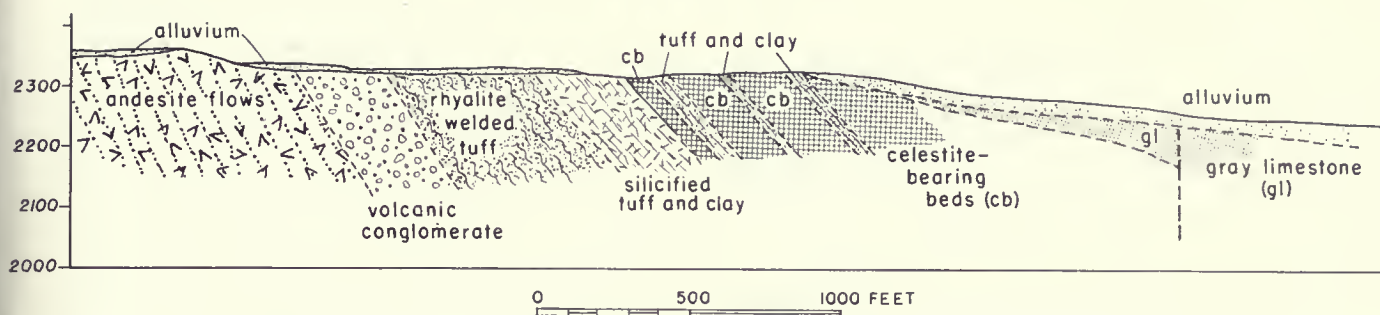


FIGURE 2. Geologic section through Cady Mountains celestite deposit, San Bernardino County. After Durrell, California Division of Mines Special Report 32, plate 9.

tions in clastic sediments, and as lenticular beds in gypsum and clastic sediments. Beds as much as 6 feet thick and several hundred feet long contain celestite with but a minor proportion of non-celestite material. Durrell (1953, p. 21) estimates the reserves to be between 250,000 and 300,000 tons of celestite rock to a depth of 50 feet. Much of it, however, is in the form of small bodies disseminated in a large volume of non-celestite material. A 2-foot bed in the western part of the area has been calculated to contain 12,000 tons of celestite rock (Moore, 1935, p. 368). The average grade of the celestite has not been determined.

Bristol Lake, San Bernardino County, contains celestite; and an attempt was made to recover it commercially during World War II. The celestite occurs as potato-shaped concretions in gypsum-bearing sandy clays that occur along the margins of the playa. The celestite concretions are most abundant on the south margin of the lake and occur within 3 feet of the surface (Durrell 1953, pp. 9-14). Strontium is present in the brine of Bristol Lake,\* and the celestite concretions are forming now.

Ten miles northeast of Barstow, strontianite deposits occur in tuffaceous clay and marl of Tertiary age. The strontianite is found on both the north and south limbs of the Barstow syncline. On the north limb most of it is contained in a 60-foot thickness of clay, limestone, and tuff. Strontianite beds up to 1 foot thick are grouped in two strontium-rich members, one 15 to 30 feet thick, the other 5 to 15 feet thick. The percentage of strontianite rock in these members ranges from zero to 23.8 percent, and the average strontium carbonate content of the strontianite rock is 73 percent. On the south limb a total thickness of 8.1 feet of strontianite rock interbedded with green clay occurs in a stratigraphic thickness of 186 feet. The strontianite on the south limb is 465 feet higher stratigraphically than that on the north limb. Reserves of strontianite rock in the two areas are estimated to be 540,000 tons (Durrell, 1953, pp. 33, 36).

Celestite nodules also occur in clay near Owl Hole Spring, San Bernardino County (Murdoch and Webb, 1940, p. 550). A vein of celestite was found in the Butts quicksilver mine, San Benito County (Laizure, 1926). Crystals of both celestite and strontianite occur in the borate mines near Barstow and Daggett.

According to Durrell (1953) the celestite and strontianite associated with lake sediments in California are replacements of the rocks in which they occur. The re-

placement was contemporaneous with sedimentation, and the source of the strontium was the connate water that permeated the sediments. Other geologists (Moore, 1935, pp. 370-374, 376, 377; Harness, 1942, p. 7) believe that the celestite and strontianite are chemical precipitates from solutions.

**Uses.** Most of the economic uses of strontium depend either on the fact that its salts impart a crimson color to a flame or on the relatively high specific gravity of strontium minerals (celestite, 3.95-3.97; strontianite, 3.7). Almost all the strontium consumed industrially is in the form of strontium chemicals produced from celestite or strontianite. Strontianite is preferred because the treatment is simpler than that required for celestite, but celestite is used in greater quantity because it is more abundant. At one United States plant (Chem. Met. Eng., 1946) celestite is crushed, ground to 90 percent minus 325 mesh, and treated with sodium carbonate in heated reaction tanks. An impure precipitate of strontium carbonate forms, which is treated to remove barium and calcium compounds. Strontium chloride, strontium hydroxide, and other strontium chemicals are made from the strontium carbonate. Small amounts of ground celestite are used for purifying caustic soda. Much of the celestite produced in Texas has been used in oil well drilling mud, but comparatively little celestite from California has been so used. At one time celestite was competitive with barite for drilling mud because the use of barite for this purpose was patented. Celestite lost this advantage when the patent expired in 1943.

The principal use of strontium chemicals is in pyrotechnics such as signal and distress flares, signal rockets, and fireworks. Strontium nitrate is the strontium chemical usually used. The following is a typical formula for red railroad fuses (Harness, 1942, p. 5):

Component	Percent
Strontium nitrate	71.1
Potassium perchlorate	13.1
Sulfur	11.1
Sawdust	4.2
Charcoal	0.5

Strontium oxalate and strontium peroxide as well as strontium nitrate are ingredients of the red tracer bullets that are used in enormous numbers in times of war. Minor amounts of strontium hydroxide are used in special greases (Worth and McClennan, 1947). Strontium compounds are used as medicinal salts and as a substitute for barite in fillers and paints, and strontium metal can be employed in vacuum tubes as getters. During

\* Analyses of the brine of Bristol Lake are given in the section on calcium chloride in this bulletin.



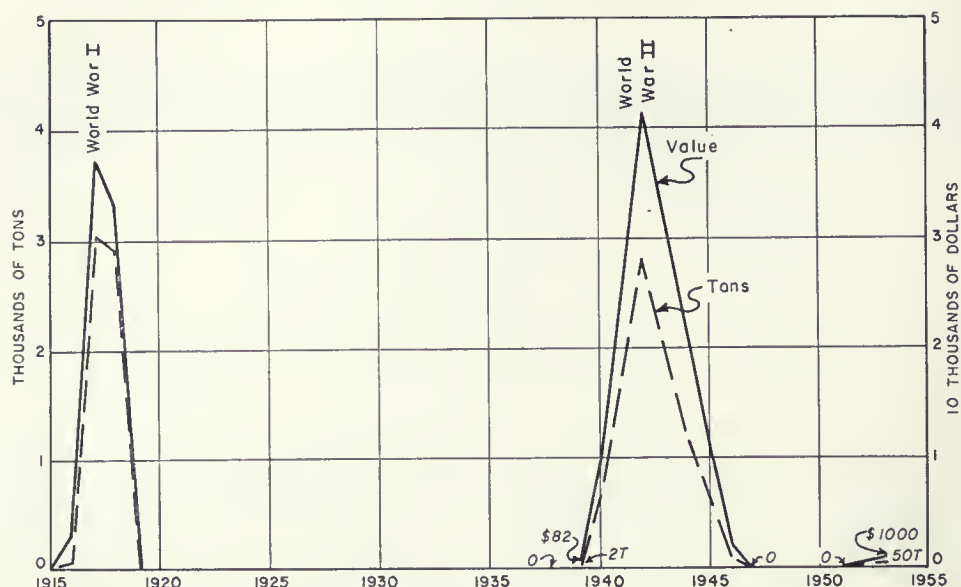


FIGURE 3. Trend in amount and value of strontium minerals produced in California. Points of change for 1941-46 are average of 2-year periods.

World War II strontium carbonate was substituted for lead carbonate in ceramic glazes, but this market no longer exists. In Europe strontium hydroxide is used in the production of beet sugar, and strontium carbonate has been added to basic open-hearth steel furnaces as a desulfurizing agent.

**Markets.** Most of the strontium chemicals used in the United States are produced by two companies, E. I. du Pont de Nemours & Company at Wilmington, Delaware, and the Foote Mineral Company at Philadelphia, Pennsylvania. Both use imported celestite. In 1955, railroad fuses were manufactured at a plant in Santa Clara County, California, from strontium nitrate brought into the state, but strontium-bearing flares for other purposes were not produced locally. Two companies in California, the Pan Chemical Company, Los Angeles, and Barium Products, Ltd., Modesto, were producing relatively small quantities of strontium chemicals from celestite for purposes such as the manufacture of grease and the refining of caustic soda. Some of the celestite was obtained from the Fish Creek Mountains deposit.

Except during World War II, when specifications were relaxed, the eastern consumers have specified celestite with a minimum  $\text{SrSO}_4$  content of 95 percent and low maximum limits for barium, calcium, and iron. Prices for crude strontium minerals are no longer quoted in trade journals, but in 1955 the price of English celestite delivered at east coast ports was about \$30 per ton (Gillson, J. L., 1955, personal communication). The nominal price of ground celestite from California, f.o.b. Los Angeles, is in the range of \$40 to \$50 per ton (Stephens, J. A., 1955, personal communication).

Under present conditions strontium minerals from California are not marketable in the eastern part of the United States. Not only do high freight charges to the distant markets adversely affect the value of the California strontium deposits, but the cost of producing a product comparable in grade to imported celestite also

is high. Most of the celestite and strontianite in California would require beneficiation. Although during World War II a substantial tonnage of celestite was shipped from the Fish Creek Mountains deposit to an eastern chemical plant, the material required careful selection to meet even the relaxed, war-time specifications. The working of a large, low-grade deposit such as that in the Cady Mountains would entail the handling of a high proportion of waste. Moreover, because the celestite rock itself is of comparatively low grade and contains finely divided, disseminated impurities, a comparatively complex beneficiation process would be required. During World War II, E. I. du Pont de Nemours & Company carried out dry table tests on the Cady Mountains material. Although concentrates containing 91-92 percent  $\text{SrSO}_4$  were obtained, the recovery was low (Gillson, J. L., 1955, personal communication). The existing market is not large enough to absorb the output of a large-scale operation, and therefore the low unit costs that are commonly realized through mechanization could not be attained.

**History of Production.** Although occurrences of strontium minerals have been known for many years, most of the large deposits were found during the early years of World War I. Perhaps the earliest discovery of a large deposit was that in the Avawatz Mountains during or prior to 1911. The Barstow deposits were discovered in 1915 by Henry Hart and T. G. Nicklin who were prospecting for borates. The Fish Creek Mountains deposit was located as a gypsum deposit prior to 1916. The first description of the Cady Mountains deposits is that of Mallery (1916) who stated that the nature of the deposit had "only recently" been realized.

Before World War I the principal strontium compounds used in the United States were strontium nitrate made in Germany and crude celestite from England. The abrupt curtailment of these sources of supply encouraged the mining of California strontium minerals and the es-



tablishment in California of plants that produced strontium chemicals from them. From 1916 to 1918 the deposits in the Cady Mountains were worked; but after 1918, when celestite from England was available again at low cost, the California mines were closed. The production from the Fish Creek Mountains has been erroneously credited to Imperial County.

During World War II the use of strontium compounds in tracer bullets and to a lesser extent in military flares increased the demand enormously, and the California mines were reopened. During 1941 and 1942 California produced 5,671 tons of strontium minerals, which amounted to about 20 percent of the national consumption. Most of this tonnage was celestite produced by the Pan Chemical Company from the Fish Creek Mountains deposit. The Rowe-Buehler Mining Company produced a smaller amount of celestite from a mine in the Cady Mountains, and during 1939, 1940, and 1941 the Strontium Carbonate Mines obtained some strontianite from the Mud (Strontianite) Hills. E. I. du Pont de Nemours & Company prepared to produce celestite from their deposit in the Cady Mountains and carried out beneficiation tests on a pilot plant scale during 1942. The project was dropped before full production was achieved because in 1943 celestite from a deposit in Mexico was placed on the market. Although the United States consumption of strontium minerals remained high, the California production began to decline. Celestite was also imported from England and Spain during World War II.

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## SULFUR AND SULFURIC ACID

By PHILIP A. LYDON

During 1954, the total sulfur production in California was equivalent to 251,900 tons of 100-percent sulfur. Only 63,300 tons of this came from sulfur deposits; the remainder was recovered from crude oil and gas. This output fell far short of supplying the numerous sulfur-consuming industries of California. Most of the sulfur used by these industries is obtained from deposits in Texas and Louisiana from which sulfur is recovered by the Frasch process. Most of the industrial sulfur consumed in this state is used to manufacture sulfuric acid. In 1954, pyrite estimated to be equivalent to 64,007 short tons of 100-percent sulfur was mined in California for this purpose (see section on pyrite in this bulletin). The markets and uses for sulfur and sulfuric acid are diverse, and include almost all phases of industrial technology.

### MINERALOGY AND GEOLOGY

Sulfur normally occurs as well-developed bipyramidal or tabular orthorhombic crystals, and as earthy or disseminated masses. The mineral has a resinous luster, a yellow or gray color, a hardness of 1.5 to 2.5, and a density of 2.05. Sulfur melts in the range 234° to 248° F., and ignites in air at a temperature of 478° F.

Native sulfur occurs in salt-dome caprock, as sedimentary beds, and as deposits associated genetically or spatially with volcanism. Most of the sulfur consumed in the United States is obtained from the Gulf Coast of Texas and Louisiana, where salt domes of various sizes have intruded great thicknesses of sedimentary rock. Many of these domes are capped by limestone, sulfur, anhydrite, and gypsum. The sulfur commonly occurs as a replacement of the limestone. Most of the zones of sulfur-bearing limestone are between 25 and 300 feet thick, and cover salt domes 100 to 2,000 acres in extent. Millions of tons of sulfur are produced annually from these deposits by means of the Frasch process, in which superheated water is injected into the deposit through part

of a bore hole while melted sulfur is pumped to the surface through another part.

Sulfur deposits of volcanic origin contribute about 3 percent of the total annual world production of sulfur. Japan, with an output of approximately 200,000 tons yearly, has been the principal producer from this type of deposit. Other countries that produce sulfur from volcanic deposits are New Zealand, Formosa, Indonesia, Italy, Spain, Mexico, South American countries along the Andes Mountains, and the United States. Production in this country has come from California, Colorado, Idaho, Nevada, Utah and Wyoming. The largest reserves of native sulfur of volcanic origin are in the Andes Mountains, where an estimated 100 million tons of ore are distributed among more than 100 deposits. Japanese reserves have been estimated at 60 million tons of 30-percent sulfur in 18 deposits (Bonfield, 1955).

Most sulfur of volcanic origin occurs as disseminations, massive replacement bodies, or veins. Disseminated sulfur is characteristic of deposits in which the ore grade is less than 50 percent, although such disseminations commonly form envelopes about richer massive replacement bodies. Large veins usually are found in the lower parts of deposits where the wall-rock is relatively unaltered. Sulfur formed by hot-spring action may be deposited in sediments at the bottoms of warm lakes. Sulfur also forms as liquid flows from volcanic vents, as cement in near-surface alluvium, and as sublimates about sulfurous gas vents.

### OCCURRENCES IN CALIFORNIA

Almost all of the native-sulfur deposits in California are associated with volcanic rocks. Production has been reported from Alpine, Colusa, Imperial, Inyo, Kern, Lake, and Shasta Counties. By far the two most productive localities have been the Leviathan mine in Alpine County and an area on the west slope of the Last Chance Range in Inyo County. The entire output of the Leviathan mine is shipped to Yerington, Nevada, where it is converted to sulfuric acid. Some of the material from the Last Chance Range has been concentrated and shipped to Los Angeles for use in the manufacture of sulfuric acid; some also has been trucked to the Bakersfield area for use as soil sulfur.

*Alpine County.* The Leviathan deposit, 9 miles east of Markleeville, consists of sulfur in equant masses, stringers, and veins, in a gray, altered, porphyritic andesite. It is hourglass-shaped in plan, with the long axis trending northward, and is flat-lying and saucer-shaped in section. The deposit has a maximum thickness of 135 feet, and is successively overlain by an average of 150 feet of kaolinized agglomerate and about 100 feet of tuff that has been silicified at the surface. Thin beds of sulfur interfinger with volcanic breccias and tuffs at points approximately a mile south and a mile west of the present pit, and large dikes of sulfur cross-cutting water-laid tuffs formerly could be seen in old underground workings.<sup>1</sup> The mined ore has averaged



FIGURE 1. Specimen of sulfur ore from Leviathan mine, Alpine County. Stringer of sulfur (greasy luster) in altered andesite. Photo by Mary Hill.

<sup>1</sup>G. H. Curtis, Professor of geology, University of California, personal communication, Oct. 1955.



about 28 percent sulfur and contains a minor amount of pyrite and traces of cinnabar. Early analyses showed that the ore contained only negligible amounts of arsenic, antimony, magnesia, lime, alumina, and mercury. A small amount of selenium is recovered during treatment of the ore.

Because it is more economical and allows better ventilation and fire-control than is possible in underground workings, an open pit is used to work the Leviathan ore body. The pit is 1,500 feet long and 600 feet wide. The large volume of overburden it has been necessary to remove has resulted in an ore to waste ratio of about 1 to 11. The sulfur-bearing rock is mined with 15-foot benches, using 5-foot vertical blasting holes in a 9- by 8-foot pattern. The altered host rock contains scattered blocks of tough, relatively fresh rock that sometimes render drilling and loading of ore difficult. In 1955, one man was operating a 2,300-pound dropball, taking the place of four or five men formerly engaged only in secondary blasting. The mined material is loaded into trucks that take it to a crushing unit west of the pit. Here it passes through a jaw crusher and an  $\frac{1}{8}$ -inch vibrating screen. Fragments less than an eighth of an inch in diameter average between 12 and 18 percent sulfur, and are rejected in order to improve the ore grade. The crushed ore is trucked to Weed Heights, near Yerington. Here it is crushed again, ground, and roasted exothermically in FluoSolids reactors. The resulting sulfur dioxide gas is cooled in a water-spray chamber and passed through a series of cyclone precipitators to remove most of the dust load. The gas is then scrubbed, passed through Cottrell mist-precipitators, and sent to a contact sulfuric acid plant.

The Leviathan mine was discovered in 1863 and was first worked for copper and gold. It was abandoned shortly afterward and remained inactive until about 1894, when it was reopened and 200 tons of copper ore were mined. Abandoned again, it lay idle until the early 1930's, when the Leviathan Sulphur Company was organized to exploit its sulfur. Development and moderate production marked the period 1933-34, after which no

further shipments were made until mid-1953. In March, 1936, the property was leased to Texas Gulf Sulphur Company and was maintained under an assignment of that lease by the Calpine Corporation of Los Angeles. In 1941, Calpine Corp. surrendered its lease to Leviathan Sulphur Co., and in 1945, Siskon Mining Corporation, a subsidiary of Texas Gulf Sulphur Co., purchased the mine. Anaconda Mining Company acquired the property in 1952 as a source of sulfur for the manufacture of sulfuric acid to be used in leaching low-grade copper ore near Yerington, Nevada. Contracts for an access road and overburden stripping were let, and mining of the ore body began in July 1953.

*Colusa County.* A small amount of sulfur has been produced from the Elgin mine, near Wilbur Springs, in Colusa County. The sulfur deposit at the Elgin mine is in shale and serpentine and lies only a short distance from the margin of a large body of serpentine. Sulfur occurs sparingly in cracks and fissures and forms a cement in the few feet of overlying soil and debris. Hot springs and sulfurous gases issue from a number of points on and near the property.

Unconfirmed reports state that unsuccessful attempts were made to produce sulfur on a commercial basis prior to 1888, and again in 1891, 1909 and 1916 (Bradley, 1918, and Logan, 1929). In 1918, two 12-foot-high steam retorts were installed, and about 3 tons of ore were mined and treated experimentally before a drop in prices after World War I forced the operation to close down. No more sulfur was mined until 1929, when a steam-retort unit and storage tank were constructed. A total of 265 tons of ore were mined before this operation was abandoned in 1932. Some exploration for sulfur was later conducted west of the mine, probably within the last 5 years, but no production has been reported. When visited in October 1955, the mine was idle.

*Imperial County.* The Full Moon sulfur deposit (Tucker, 1926) is on the southwest slope of the Chocolate Mountains in north-central Imperial County. It is a surficial deposit in which sulfur occurs in disseminations and seams in tufa. It was located in 1928, and subsequently was developed by several open pits, shallow shafts, and short tunnels.

The Coyote Mountain gypsum and sulfur deposit, 7 miles north of Coyote Wells, consists of brown, iron-stained gypsum mixed with 2 to 5 percent elemental sulfur. The sulfur occurs in slightly greater abundance along a northeastward-trending fault zone that cuts granite, schist, and limestone. Development has been by means of pits and an open cut in the hillside. Vesubio Mining Corporation, Ltd., has leased this property since the early 1930's. Soil sulfur and refined dusting sulfur were produced by this company at their plant in Calexico from 1940 to 1942. However, ore for this plant came from the company's mine in Baja California, and not from Imperial County as has been previously reported (Sampson and Tucker, 1942). Equipment at the Baja mine was damaged by fire in 1942, and raw material for the Calexico plant has since been secured from Texas.

*Inyo County.* The sulfur claims on the west slope of the Last Chance Range, east of Big Pine, yielded almost a third of the native sulfur produced in California be-



FIGURE 2. Leviathan open-pit mine, Alpine County. Sulfur ore-body is overlain by kaolinized agglomerate and tuff. Upper surface of orebody marked by line. View to northeast.



tween 1865 and 1954 (see table 2). The most consistently active claims, and the ones most extensively developed, are the Crater group of six claims and the Gulch group of ten claims.

These claims lie in a depression between two northward-trending, block-faulted ridges composed of Paleozoic sedimentary rocks. Several north-trending faults cut Tertiary volcanic and sedimentary rocks in the depressed area, and two principal zones of sulfur mineralization are parallel to and bounded by these faults (Lynton, 1938). These zones are each about 2,500 feet in length, and have irregular widths. Most of the sulfur occurs as steeply dipping veins of various sizes, as shallow, flat-lying bodies the disposition of which is probably controlled by fracturing in the rhyolite, and as disseminated matter in bodies with indefinite boundaries. Wallrock observed on the surface is a dense, white, silicified rhyolite, whereas drill holes and underground workings revealed wallrock of gypsum, conglomerate, and chert (Lynton, 1938). Scattered beds of essentially barren pumiceous tuff also are present. The Crater claims lie astride both zones of mineralization, whereas the Gulch claims immediately to the south embrace a smaller mineralized area that appears to be separate from the other two zones.

Mining activity to date has centered around three ore deposits. The largest of these, on Crater No. 1 in the western mineralized zone, was once worked by a 200-foot shaft and a few hundred feet of drifts. These workings caved in during the early 1940's, so that a shallow open cut provided the only access to the ore in 1955. A large open pit on Crater No. 2, in the eastern zone of mineralization, was used to work a shallow ore body after limited underground work proved to be hazardous. An open cut on Gulch No. 1 was being used in 1955 to extract sulfur for use as an agricultural mineral.

Sulfur in the open cut on Crater No. 1 occurs as seams in finely fractured, partially bleached siliceous rhyolite and in tuff containing black obsidian fragments. High-grade ore is confined to a fracture that strikes southeast and dips steeply northeast, occurring in a 4-foot width of massive, almost pure sulfur. Away from this vein, many sulfur seams have vugs in which crystals with well-formed faces occur. In the pit on Crater No. 2, sulfur occurs in small veinlets, in microscopic seams, and disseminated in the silicified-rhyolite wallrock. A thick, barren bed of pumiceous tuff overlies the rhyolite. Ore on the walls of the pit is low grade. A 54-foot drill hole at the bottom of the pit, however, is reported<sup>2</sup> to have encountered an unspecified amount of high-grade ore.

The principal known deposit of the smaller mineralized area is on the Gulch No. 1 claim, where sulfur occurs in a southeast-dipping, northeast-trending zone in silicified rhyolite. Pure, yellow, native sulfur forms broad seams and patches in this zone, which averages 60 percent elemental sulfur. Overburden is variable in thickness and consists of impure gypsum. The deposit is worked by an open cut. Approximately 30 feet of its depth, 40 to 50 feet of its width, and 150 feet of its length is or was in ore.

Open cuts, pits and trenches elsewhere in the area reveal very low-grade ore in which sulfur occurs as thin

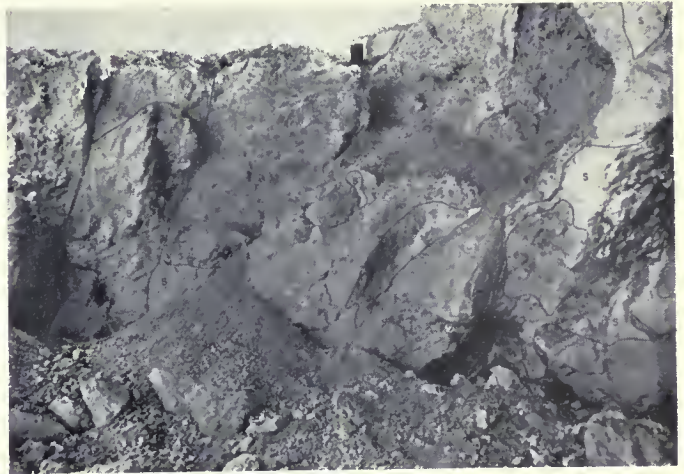


FIGURE 3. Southeast face of open cut on Crater No. 1. Last Chance Range, Inyo County. Steeply dipping vein of sulfur is in a shear zone (F-F). Richest areas of sulfur mineralization are indicated by "S."

seams in a dense, fractured, silicified rhyolite. There is little or no disseminated sulfur between these seams. The rhyolite is commonly overlain by a thin bed of pumiceous tuff.

The sulfur deposits of the Last Chance Range have a history of ownership and attempted production dating back to 1917. The peak period of activity was from 1928 to 1943. Early in this period, Pacific Sulphur Company sank a 200-foot shaft on Crater No. 1, erected several buildings, and completed a churn-drilling program. Later, an open pit was started on Crater No. 2, and several steam retorts were built. In all, the equivalent of more than 48,000 tons of 100-percent sulfur was produced during these years. Since 1945, intermittent attempts at mining in this area have yielded only a few thousand tons of sulfur. The principal deterrents to sustained production from the Last Chance Range have been high shipping costs and lack of water at the mine site.

**Kern County.** As early as 1893, small deposits of sulfur were reported east of Maricopa, in the Sunset oil district (Watts, 1893). Sulfur in this area is reported to be a gray amorphous material, which occurs as a cement in soil and disseminated through sedimentary rocks containing clay, gypsum, and bituminous matter.

**Lake County.** The Sulphur Bank mine, the Canary Hill mine at Chalk Mountain, and the Seward or Anschwitz property have been of interest at one time or another because of their sulfur content.

The Sulphur Bank mine is situated on the eastern arm of Clear Lake. In the mine area, contorted, slightly metamorphosed Franciscan shale and sandstone are unconformably overlain by lake beds and by a Recent augite andesite flow capped by 25 feet of white, powdery, opaline silica formed by leaching. Gypsum and sulfur have been deposited in open spaces in this caprock. A major northeast-trending fault zone is intersected by a series of northwest-trending faults with minor displacement. Cinnabar, pyrite, and hydrothermally altered rock occur principally along the fault zones, where hot springs and fumaroles still are active (Everhart, 1946).

<sup>2</sup>R. E. Kitching, Bakersfield, personal communication, Nov. 1955.





FIGURE 4. Open cut on Gulch No. 1, Inyo County, follows narrow, southeast-dipping zone of sulfur mineralization. View to east.

This mine, which was operated by California Borax Company, yielded 941 short tons of sulfur during the period 1865-68, and then closed down because of a fall in the price of sulfur, and because the cinnabar content made refining increasingly difficult. The mine was reopened in 1873, and has since been worked only for quicksilver.

The Chalk Mountain sulfur deposit is near Cache Creek about 4 miles north of State Highway 20. Traces of sulfur-bearing material, consisting mostly of sulfurous alum salts, occur in a white, bleached andesite (?) in which feldspar laths are still visible. Moderate amounts of hydrogen-sulfide gas issue from the rock in a number of places. In 1951, an investigation<sup>3</sup> revealed that sulfur occurred principally as a cement in shallow debris and along joints in the wall-rock. The highest-grade material exposed at that time contained approximately 15 percent sulfur.

This property, first worked for sulfur prior to 1890, was located by Caryl Dow in October, 1951. Shortly afterward it was leased to Chemi-Cal Sales Corporation. Intermittent attempts at development failed to uncover substantial amounts of ore, and in January 1954, the lease was terminated. The mine was idle when visited in October 1955.

The Seward or Auschwitz (Averill, 1947) property and adjacent claims are approximately half a mile south of the Kelseyville-Lower Lake highway near the S-Bar-S ranch. The principal deposit consists of sulfur disseminated in a cross-bedded, highly altered body of tuff which overlies an obsidian flow. The tuff apparently was deposited in a cup-shaped depression in the obsidian. Fragments of pumice and obsidian occur in the tuff, which strikes northeast and dips gently to the north-

west. Sulfur is rather uniformly distributed throughout the wall-rock of tuff, but widely spaced crevices are filled with relatively rich concentrations of the mineral. The deposit averages about 10 percent sulfur, and appears to measure less than 100 feet in its longest dimension.

These claims are owned jointly by the Lower Lake Minerals Corporation and Alvin Seward of Kelseyville, who have formed the Lake County Minerals Corporation. Pacific Sulphur Company was sub-leasing the property in late 1955. There has been no commercial production from this property, although a few tons were removed for experimental use as soil sulfur. Two untimbered adits, 20 and 40 feet long, respectively, penetrate a low, open-cut face on the south side of the principal deposit. A shaft, once 50 feet deep, was filled in 1950 when the open cut was made.

*Shasta County.* The Supan Sulphur Works, situated in Lassen Volcanic National Park, were discovered and located in 1865. The property was patented in the 1920's, and was operated as a tourist attraction after 1940. In 1951, the Sulphur Works were acquired by the U. S. Government and are now a part of the National Park System. Steam vents, mud pots and hot springs are the main features of interest here. Sulfur is deposited from gases as sublimated crusts, and from hot water as crusts and impregnations. Old reports (Day and Allen, 1925) state that sporadic mining activity occurred at this locale prior to 1900. The total production, however, could not have been more than a few tons.

#### BYPRODUCT SULFUR AND SULFURIC ACID

More than half of the sulfur-equivalent produced in California during 1954 was derived from the treatment of sour or sulfurous crude oils and gases, and waste-acid sludges from petroleum refineries. A crude oil is classified as sour if it contains 0.05 cubic foot or more dis-

<sup>3</sup>Salem J. Rice, Division of Mines, personal communication, Nov. 1955.



solved hydrogen sulfide per 100 gallons of oil. A sulfurous crude oil is one that contains either dissolved elemental sulfur or hydrogen sulfide. The removal of hydrogen sulfide from sour crude oil is desirable because such oils represent an unnecessary fire hazard, are often lethally poisonous, and may cause extensive corrosion damage to refinery equipment. Moreover, an additional 1 to 1½ cc of tetraethyl-lead fluid per gallon are required to overcome the poor lead susceptibility of gasoline derived from untreated sour crude oil.

A further reason for removing hydrogen sulfide and sulfur from crude oil is to prevent their discharge into the atmosphere as sulfur dioxide when refinery wastes are burned. Although sulfur dioxide released to the air in this manner is an air pollutant, no data are available to indicate that it contributes to the formation of smog (Went, 1955).

Petroleum refineries in the Los Angeles and San Francisco Bay areas yield both sulfuric acid and elemental sulfur as byproducts of gas and oil processing. In California, during 1955, there were at least 8 sulfuric-acid plants, 10 hydrogen-sulfide recovery units and 8 plants that produced liquid sulfur. Minor amounts of liquid sulfur dioxide and liquid hydrogen sulfide also were produced. Some oil companies operated hydrogen-sulfide recovery units and liquid-sulfur plants at their own refineries, whereas other companies shipped recovered hydrogen sulfide or waste acid sludges to a sulfuric-acid plant operated by another concern and received an equal value of sulfuric acid in return. These sulfuric-acid plants utilize as raw materials hydrogen-sulfide gas, smelter fumes, pyrite, and Frasch sulfur. Because the quality and quantity of sour gases received by a sulfuric-acid plant vary from season to season, Frasch sulfur is often kept on hand and used to maintain a steady and therefore more economical volume of production. The amount of California-derived raw material that such plants utilize is difficult to determine.

The byproduct-sulphur industry in California began in the late 1930's and is still growing. A new sulfur-recovery unit was placed in operation during 1955, and a liquid-sulfur plant was under construction. It is estimated that the equivalent of 188,600 short tons of 100-percent sulfur was produced as a byproduct in California during 1954. This does not include the sulfur-equivalent derived from pyrite, nor does it include that obtained from out-of-state raw material.

One successful sulfur-recovery unit near Los Angeles introduces hydrogen sulfide and a controlled amount of air into a burner, where the hydrogen sulfide is partially oxidized. The hot combustion gases pass through a waste heat boiler, which utilizes reaction heat to generate steam, and then into a catalytic converter in which oxidation is completed. From here the gases go into a condenser and then to a reheater and a second converter-condenser unit. A scrubbing tower removes the last of the sulfur. Waste gases are then burned and discharged to the atmosphere. As it is condensed, liquid sulfur is withdrawn from the waste heat boiler, the converters, condensers, and scrubber. It is collected, stored, and shipped from the plant in the liquid state.

The most widely used processes for the removal of hydrogen sulfide from sour gas involve the use of ethanalamine solutions. These are organic bases that

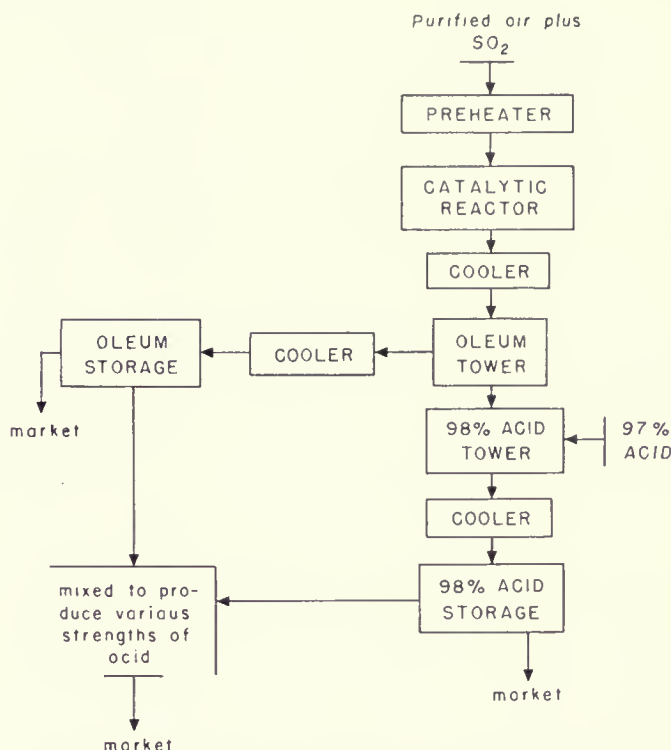
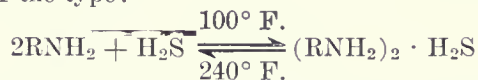


FIGURE 5. Generalized flow sheet of the contact process for manufacture of sulfuric acid.

react chemically with acidic gases at normal temperatures and effect their removal from other gases. In these reactions, chemical bonds are so loosely attached that the process behavior is similar to that of absorption. The resulting complex organic compounds are unstable at temperatures in the range 240° to 300° F. Thus, circulating ethanalamine solutions in one column can be contacted with sour gas at ordinary temperatures, while in a second column the amine solution is regenerated and acidic gas recovered at boiling-point temperature and reduced pressure. The reversible reaction involved is of the type:



This process can accomplish a nearly complete removal of carbon dioxide as well as of hydrogen sulfide, and produces a sweet gas that readily meets the usual specifications of 0.25 grains maximum H<sub>2</sub>S per 100 cubic feet of gas. Aqueous diethanalamine or monoethanalamine solutions may be used for removal of hydrogen sulfide and carbon dioxide, or a mixture of an ethanalamine, diethylene glycol and water may be used for simultaneous sweetening and dehydration.

#### SULFURIC ACID MANUFACTURE

Pure, 100-percent sulfuric acid is a colorless, odorless, heavy, oily liquid. Commercial sulfuric acid ordinarily has a density of 66° Baumé and contains 93 percent H<sub>2</sub>SO<sub>4</sub>. One gallon weighs 15.2 pounds and contains 4.64 pounds of sulfur. Sulfuric acid is capable of dissolving large quantities of sulfur trioxide, forming various grades of oleum. When oleum solutions are mixed



Table 1. Production of native-sulfur ore in California.  
(Short tons, unspecified grade)

County totals, 1865-1954			
Alpine.....		450,968	
Colusa.....		268	
Inyo.....		60,729	
Kern.....		385	
Lake.....		941	
Total.....		513,291	
Statewide totals			
1865-68.....	941	1939.....	9,287
1869-1915.....	minor	1940.....	5,933
1916-17.....	20	1941.....	10,032
1918-19.....	23	1942-43.....	5,286
1920-22.....	200	1944-45.....	0
1923-24.....	185	1946.....	760
1925-28.....	0	1947-48.....	1,787
1929-31.....	265	1949-50.....	2,700
1932-33.....	1,217	1951-52.....	1,925
1934.....	6,671	1953-54.....	451,300
1935-36.....	5,308		
1937-38.....	9,451	Total.....	513,291

with water, the dissolved oxide combines with the water to form more sulfuric acid.

Sulfuric acid is produced commercially by the contact and chamber processes. In both methods, the raw material is sulfur dioxide, which may be obtained by burning elemental sulfur, pyrite, or hydrogen sulfide. The contact process is the more widely used of the two because it allows savings in space, makes more efficient use of raw material, and has a faster reaction rate. In this process, gases containing 7 to 10 percent sulfur dioxide and 11 to 14 percent oxygen are preheated and then contacted on a platinum or vanadium pentoxide catalyst in a converter. Sulfur trioxide leaves the converter, is cooled and enters an oleum tower where it is absorbed by sulfuric acid. Some of the reacted product leaves this tower and goes to an oleum storage unit, while most of the rest is introduced into a 98-percent acid tower where it is concentrated to a marketable strength.

The chamber process involves the use of nitric oxide to effect partial oxidation of hot sulfur-dioxide gas. The resulting mixed gases then go to a series of lead chambers where most of the sulfur dioxide is oxidized to sulfur trioxide and hydrated by water spray to sulfuric acid. The chamber acid is then scrubbed and concentrated to produce a marketable acid.

All the pyrite mined in California for its sulfur content has been used in the manufacture of sulfuric acid. Such ore, produced from Alameda and Shasta Counties, has over the years averaged approximately 50 percent sulfur. California has yielded 5,104,164 short tons of pyrite ore from 1898 to 1954. This is equivalent to 7,401,816 tons of 100-percent sulfuric acid, or to 2,552,308 tons of sulfur (see section on pyrite in this volume).

#### PRODUCTION

United States production of equivalent sulfur in 1954 is estimated at 7,364,500 short tons (Chemical Engineering, 1955), of which about 5 percent was produced in California. Approximately 80 percent of this amount came from the 13 Frasch sulfur mines of the Gulf Coast, about 10 percent came from smelter and refinery

Table 2. Production of native-sulfur ore in California.  
(Recolculated to short tons, 100 percent sulfur.)

County totals, 1865-1954			
Alpine.....		127,053	
Colusa.....		258	
Inyo.....		50,246	
Kern.....		172	
Lake.....		894	
Total.....		178,623	
Statewide totals			
1865-68.....	894	1939.....	8,321
1869-1915.....	minor	1940.....	5,361
1916-17.....	8	1941.....	9,470
1918-19.....	10	1942-43.....	5,022
1920-22.....	86	1944-45.....	0
1923-24.....	86	1946.....	613
1925-28.....	0	1947-48.....	447
1929-31.....	256	1949-50.....	675
1932-33.....	1,096	1951-52.....	674
1934.....	5,725	1953-54.....	126,589
1935-36.....	4,557		
1937-38.....	8,733	Total.....	178,623

gases, 6 percent from pyrites, 3 percent from sludge conversion and 1 percent from low-grade, native-sulfur ores. The largest domestic producer was Boling Dome in Texas, operated by Texas Gulf Sulphur Company. The next most important producers were Freeport Sulphur Company's Grade Ecaille and Garden Island Bay deposits in Louisiana.

An aura of uncertainty has almost always attended published statements concerning production of native sulfur in California. Old, unpublished records and previously published reports, for example, often make no distinction between long and short tons or between unconcentrated ore and refined sulfur cake. Original production reports, however, commonly show the unit price or the total value of ore shipped during a given period of time, and thereby suggest the grade. Sulfur production in California is summarized in tables 1 and 2.

#### UTILIZATION

Of the total supply of sulfur available in the United States in 1954, approximately 24 percent was exported, 61 percent was used in domestic acid manufacture, and 15 percent was applied to domestic non-acid uses (Chemical Engineering, 1955). The domestic consumption pattern of sulfur in 1954 showed little change from that of recent years. Fertilizer accounted for 33 percent; chemicals, 18 percent; pigments and pulp,  $7\frac{1}{2}$  percent each; iron and steel, 7 percent; ground- and refined-sulfur uses, 5 percent; carbon bisulfide and rayon and film,  $4\frac{1}{2}$  percent each; petroleum, 3 percent; and miscellaneous uses, 10 percent (Chemical and Engineering News, 1955).

The principal uses of sulfuric acid are in the manufacture of fertilizers, chemicals, paints, pigments, rayon, film, coal products and industrial explosives, petroleum refining, iron and steel pickling, and textile processing. Fertilizers and insecticides, the manufacture of pulp and paper, explosives, dyes, rubber, and the preparation of food products are the principal non-acid uses of sulfur.

In the preparation of superphosphate fertilizers, washed phosphate rock is treated with sulfuric acid to make the phosphate available to plants and to provide



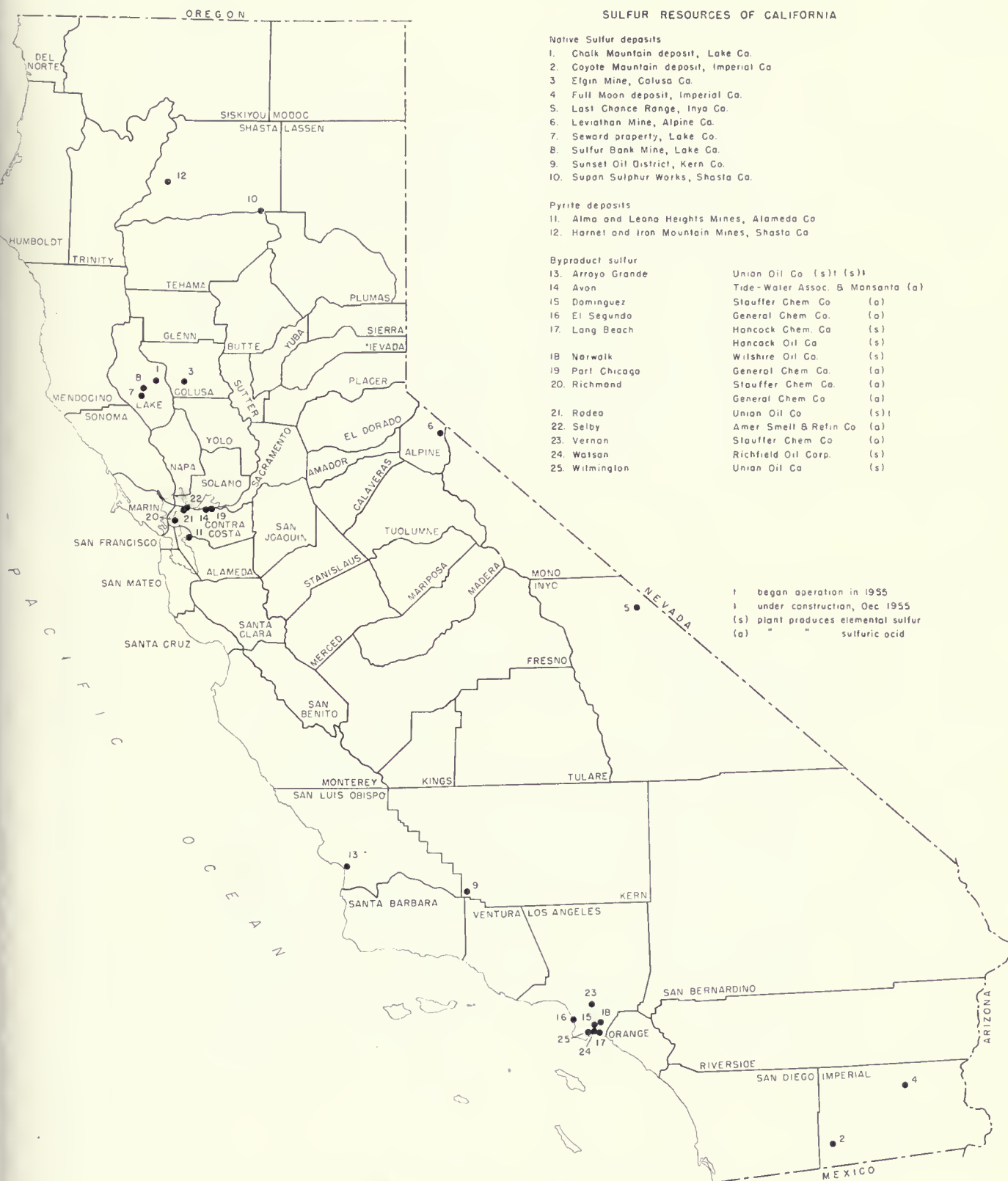


FIGURE 6. Map of California, showing sulfur resources.



sulfur, an essential plant food. Nitrogenous constituents released during the coking of coal pass off as ammonia, and these gases are scrubbed with sulfuric acid to produce ammonium sulfate. In the paint and pigment industries, titaniferous ores are dissolved by sulfuric acid and then pure titanium dioxide is precipitated by hydrolysis. In the viscose process for making rayon, the viscose is precipitated in a sulfuric-acid solution. The manufacture of nitro-cotton, from which motion-picture film is made, consumes large amounts of sulfuric acid. It is also used in purifying coal-distillates, such as toluol and benzol. In the nitration process for the manufacture of nitroglycerin, nitric acid is used in the presence of concentrated sulfuric acid. Propellant explosives for military use contain large amounts of nitro-cotton, which is made by nitrating cellulose in a bath of mixed nitric and sulfuric acids. In petroleum refining, sulfuric acid is used to remove tars, gums, and other materials that would form corrosive end-products, as, for example, in the manufacture of high-octane components for aviation gasoline. The metallurgical industry uses sulfuric acid to remove scale formed during the various steps of rolling and annealing iron and steel, as a bath in electrolytic-zinc production, to leach low-grade copper ores, and in the manufacture of copper sulfate, an activator used to separate sphalerite in lead-zinc ores. Sulfuric acid is also used in the various operations of washing, bleaching, shrinking, and dyeing of textiles.

Sulfur, as a dust or in sprays such as lime-sulfur solutions or wettable sulfurs, is used to control pests that attack fruit trees as well as truck and field crops. Ground sulfur is used as a soil additive to minimize alkalinity or to correct sulfur deficiency. Soil rich in selenium and deficient in sulfur favors the growth of plants which selectively absorb selenium and which are noxious to cattle, horses, and other animals. Sulfur, when added to such soil, acts as an inhibitor to selenium absorption.

Sulfur as a conditioner of alkali soils is used in many parts of California. Alkali soils are abnormal because they contain an excess of soluble salts and/or exchangeable (adsorbed) sodium ion. If the content of soluble salts is low and that of exchangeable sodium ion is high, the physical condition of the soil is usually unfavorable for either plant growth or tillage operations. To reclaim the soil, excess salts must be removed and sodium and magnesium ions, if excessive, must be replaced by calcium ion. Although gypsum is useful in this respect, it is only slightly soluble in water and requires intensive irrigation for maximum efficiency. The effectiveness of sulfur for such use depends on its rate of oxidation and on the presence in the soil of a calcium compound that is soluble in weak sulfuric acid. One or more species of sulfur-oxidizing bacteria are widely distributed in alkali soils, and their action on sulfur leads eventually to the formation of sulfuric acid, which is primarily responsible for the chemical reactions that occur when sulfur is applied to the soil. It follows from this that sulfuric acid applied directly in irrigation water would also be effective in alkali-soil reclamation. In spite of the high costs involved, this use of sulfuric acid has steadily increased in California.

The California State Bureau of Chemistry lists 23 firms registered in 1954 as dealers in soil sulfur and lime-sulfur solutions. The actual sulfur content of soil sulfur used in California that year ranged from 28 to 99.5 percent. Almost all dusting and wettable sulfurs sold in California during 1954 contained between 95 and 99 percent sulfur; lime-sulfur solutions averaged 30 percent calcium polysulfide and 1.5 to 5 percent calcium thiosulfate; DDT-sulfur mixtures contained 5 to 10 percent DDT and 50 to 75 percent sulfur. During 1954, sales of soil sulfur and agricultural sulfuric acid in California amounted to 9,841 and 2,245 tons, respectively.

In the sulfite process of pulp manufacture, sulfur or pyrite is burned to form sulfur dioxide, which is reacted with limestone in the presence of water to form a mixture of calcium bisulfate and sulfurous acid, in which wood chips are digested. Between 200 and 300 pounds of sulfur are required per ton of pulp. In 1949, Pacific Coast requirements of sulfur for this use were 145,000 tons.

The proportion of sulfur used in rubber manufacture varies with the product. Hard rubber used in storage-battery cases may contain as much as 30 percent sulfur, whereas rubber used in tire stock may contain only 1.5 percent. Small amounts of sulfur are still used in the manufacture of black-powder explosives, although nitroglycerine in dynamite or other forms has almost entirely replaced this material.

Table 3. *Estimated annual consumption of sulfur in northern California industry, 1948 (Eipper, 1950).*

Consumption (short tons)	Commodity	Industry
10,000.....	Sulfur.....	Pesticides
2,000.....	Sulfur.....	Food processing
200.....	Sulfur.....	Rubber manufacture
1,000.....	Sulfur dioxide.....	Petroleum refining
140,000.....	Sulfuric acid.....	Petroleum refining
10,000.....	Sulfuric acid.....	Other industries

Table 4. *Agricultural minerals consumed in California.\**  
(short tons).

	Soil sulfur**	Sulfuric acid
1924-30.....	6,790	0
1931-40.....	23,092	0
1941-50.....	196,824	21,973
1951-54.....	42,256	14,188
Totals.....	268,962	36,161

\* (California Bur. Chemistry, 1954.)

\*\* Sulfur-equivalent not known.

In California, the consumption pattern of sulfur and sulfuric acid is complex because of the diversity of agricultural and industrial enterprise. Sulfur and sulfur-equivalent export-import records for the state are not kept by any central agency. Such information is held largely by the individual companies actually involved in the sale, purchase, and transportation of pertinent goods. A few estimates of sulfur consumption in California are available, however. Table 4 lists the agricultural sulfuric acid and soil sulfur used in this state since 1924. Table 3 lists estimates made of the consumption of sulfur and



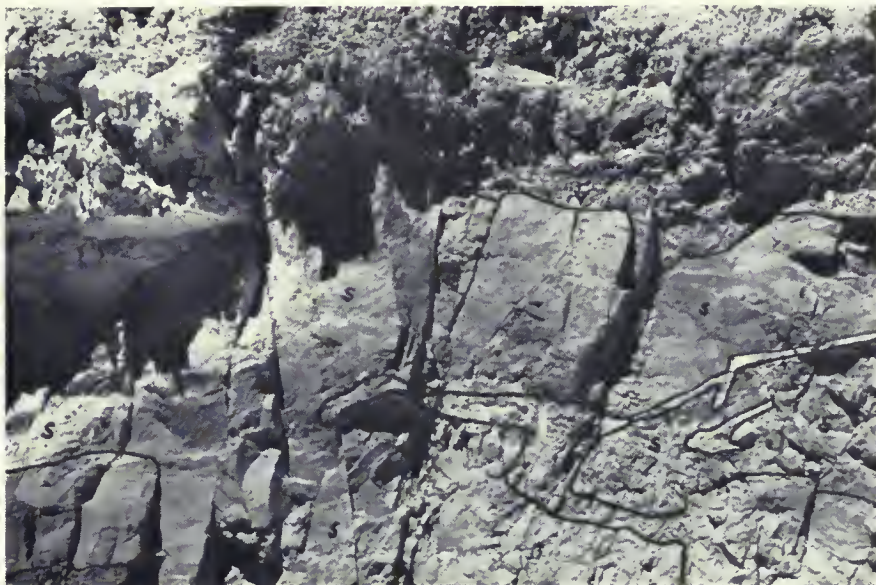


FIGURE 7. Detail of sulfur(s) in rhyolite on southwest wall of open pit, Crater No. 2 claim, Last Chance Range deposits, Inyo County.



FIGURE 8. Detail of sulfur(s) and black quartzite on west wall of open pit, Crater No. 1 claim, Last Chance Range deposits, Inyo County.



related compounds in northern California industries during 1948.

### MARKETING

The following prices were in effect during the last week of December 1955 (Oil, Paint and Drug Reporter):

SULFUR, crude, bulk, f.o.b. Texas-Louisiana mines, contract, per long ton -----	\$26.50
SULFURIC ACID, 99-100 percent, tanks, f.o.b. works, per ton -----	\$23.95
PYRITES, Canadian, f.o.b. works, per long ton -----	\$3.00- 5.00
PYRITES, domestic, consumer's plant, per long ton -----	\$9.00- 11.00

During this time, soil sulfur averaging 60 percent elemental sulfur was sold in the Bakersfield area at \$40-\$45 per ton.

Elemental sulfur produced at recovery plants processing sour gas is usually sold at a price competitive with that of Frasch sulfur, although the actual price at which it is sold is controlled almost entirely by local market conditions. Because the cost of shipping sulfuric acid is high, plants producing this material are located close to the consumers; the ultimate price also is determined by local conditions.

In the San Francisco and Los Angeles areas, sulfuric acid, 99 percent, tanks, f.o.b. works, generally was sold early in 1956 for \$26.45 per short ton. The cost of Gulf Coast sulfur delivered in bulk at either Los Angeles or San Francisco is \$1.37 per hundred weight in carload lots of 80,000 pounds, or \$27.40 per short ton.

Soil sulfur sold in California is sold as an agricultural mineral. The California Bureau of Chemistry defines an agricultural mineral as a mineral substance containing a total of less than 5 percent available nitrogen, potash, and phosphoria. Agricultural minerals sold within the state must be registered with the Bureau of Chemistry by the seller, and any guarantees made for the material must be declared. Although existing laws permit any percentage of contained sulfur in soil sulfur, the minimum amount of sulfur actually present in the particular lot being sold must be clearly shown on a label. Periodic checks are made by the Bureau of Chemistry to assure that agricultural minerals are not being mislabeled and that guarantees are being met.

The miner of sulfur deposits in California has always been confronted with certain problems, chief among which are the general low grade of California deposits, the high cost of transportation to suitable markets, and competition from cheaper, out-of-state material. Statistics published by the Bureau of Chemistry (table 4) indicate that there has been a firm market for soil sulfur in this state during the last decade. Nevertheless, the cost of mining, treating, and transporting soil sulfur is so

great compared to the market value that usually only the higher-grade material can be worked profitably. In general, the owner of a sulfur deposit in California who wishes to develop his property should mine the sulfur cheaply (preferably by open pit) and sell it for agricultural purposes as short a distance from his deposit as is feasible. The grade of sulfur he can afford to mine is determined by the costs of mining and the current market value of his product.

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## TALC AND SOAPSTONE

BY LAUREN A. WRIGHT

The annual production of talc and soapstone in California has increased from a few tens of tons in the early 1900's to 118,288 tons in 1954 to place the state second to New York as a source of these commodities. An estimated total of 1,830,000 tons of talc has been produced in California through 1956. At least nine-tenths of this output has been obtained from deposits in a 200-mile belt, along the eastern margin of California, where large quantities of talc have formed as alterations of pre-Cambrian and Paleozoic strata. The remainder consists mostly of soapstone quarried along the western foothills of the Sierra Nevada and in Los Angeles County. The talc mined in California is of numerous varieties, and is employed in many ways, but its main uses are in the manufacture of ceramic bodies and paint. It is consumed mostly within the state, but large tonnages also are shipped to out-of-state markets. Talc of steatite grade, which is unusually pure, is shipped to the eastern United States and used in the manufacture of high-frequency electrical insulators.

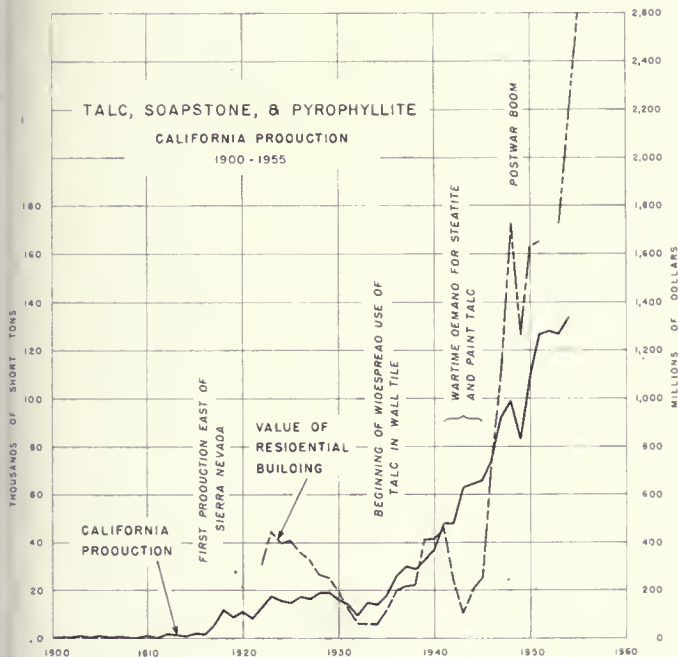


FIGURE 1. Chart showing production of talc, soapstone, and pyrophyllite in California from 1900 to 1955, compared with value of residential building in California from 1900 to 1955. Building figures 1939-55 from U. S. Dept. Commerce; earlier figures approximate.

**Mineralogy and Terminology.** To the mineralogist "talc" is a distinct mineral species with a composition of  $\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$ , but in commercial usage the term also alludes to a mixture of minerals most of which are high-magnesium silicates. The mineral talc is ordinarily, but not necessarily, a prominent constituent of commercial talc. Other minerals common in such mixtures include tremolite ( $\text{Ca}_2\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$ ), serpentine (a hydrous magnesium silicate), chlorite (an alumino-silicate of iron and magnesium), anthophyllite ( $(\text{Mg},\text{Fe})_7\text{Si}_8\text{O}_{22}(\text{OH})_2$ ),

olivine ( $(\text{Mg},\text{Fe})_2\text{SiO}_4$ ), carbonate minerals, and quartz. The chemical compositions of many commercial talcs, therefore, differ markedly from the composition of the pure mineral. For many uses the other minerals are either beneficial or harmless, but for uses such as in the manufacture of pharmaceuticals, cosmetics, and electrical insulators, they constitute impurities.

The mineral talc ordinarily can be distinguished by an extreme softness, a soapy feel, a flaky habit and a marked inertness. Most aggregates of pure talc grains are friable, but some are blocky. The properties that most determine the usefulness of the mineral talc are whiteness when ground and fired, softness and smoothness, good lubricating power, chemical inertness, a high fusion point, low electrical conductivity, and high absorption of certain types of greases and oils.

In current industrial usage the term "steatite" ordinarily is applied to high-purity talc whose maximum allowable proportions of  $\text{CaO}$ ,  $\text{Fe}_2\text{O}_3$ , and  $\text{Al}_2\text{O}_3$  are 1.5 percent, 1.5 percent and 4.0 percent respectively, and which is suitable for use as an ingredient in the manufacture of high-frequency electrical insulators (Klinefelter, et al., 1945).

Talcose rock from which bodies can be machined is known by the general terms "block talc," or "lava." "Block steatite talc" is block talc that meets steatite specifications. A small tonnage of massive chlorite, which resembles blocky talc in its physical appearance, is mined in California under the general designation of talc. The term "soapstone," as most commonly used, refers to a blocky material rich in the mineral talc, but containing impurities that prevent its use as a high-grade commercial talc.

The name "hard talc" commonly is applied by miners in California to commercial talc that contains a high proportion of tremolite, whereas "soft talc" is applied to crumbly talc schist of high quality. Ground and bagged commercial talcs ordinarily are referred to by trade names, and most of them consist of blends of several types of crude commercial talc. As talcs also are designated by the use to which they are best suited, such terms as "paint talc," "ceramic talc" and "cosmetic talc" are widely applied to crude materials as well as to milled and blended products.

**General Geology.** Most deposits of commercial talc are alterations of high-magnesian rocks, principally dolomite, dolomitic limestone, and ultrabasic igneous rocks, but in a few areas mineable concentrations of talc have formed as alterations of other rocks including quartzite, granite, and low-magnesium limestone.

The alteration of ultrabasic igneous rocks to talc involves essentially the hydration of olivine and pyroxene to hydrous magnesium silicate minerals of which talc ordinarily appears to be the last to form. The mineral serpentine commonly forms as an intermediate product in this progressive hydration. In some deposits the additive water appears to have originated in the ultrabasic magma itself; in others it may have been derived from other intrusive bodies at depth. Talc deposits associated with ultrabasic rocks occur in the eastern United States



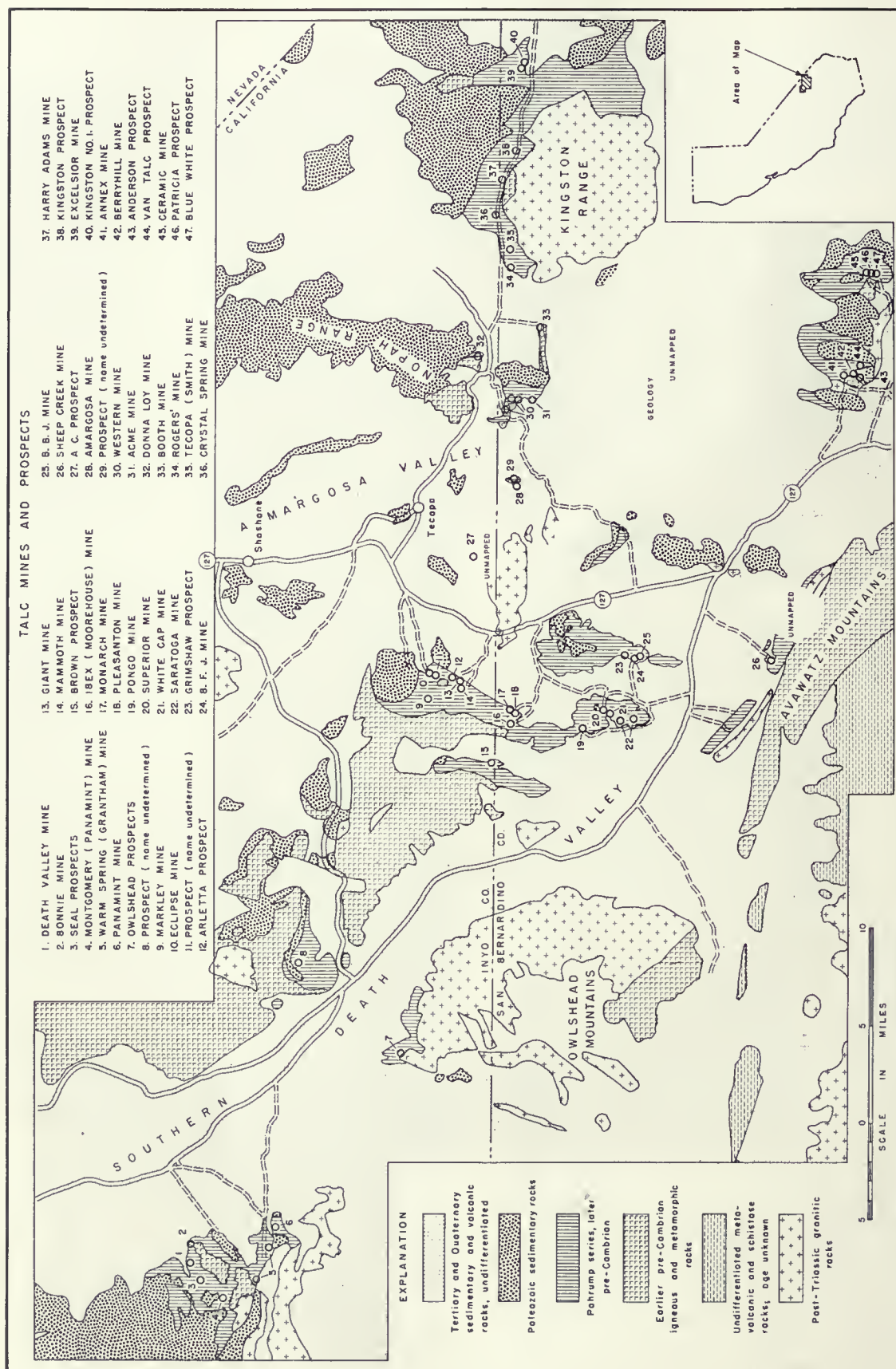


FIGURE 2. Map of the southern Death Valley-Kingston Range region showing the distribution of major rock units and location of talc mines and prospects. Geology modified from Noble and Wright (1954), Kupfer (1954), and Hewett (1956).



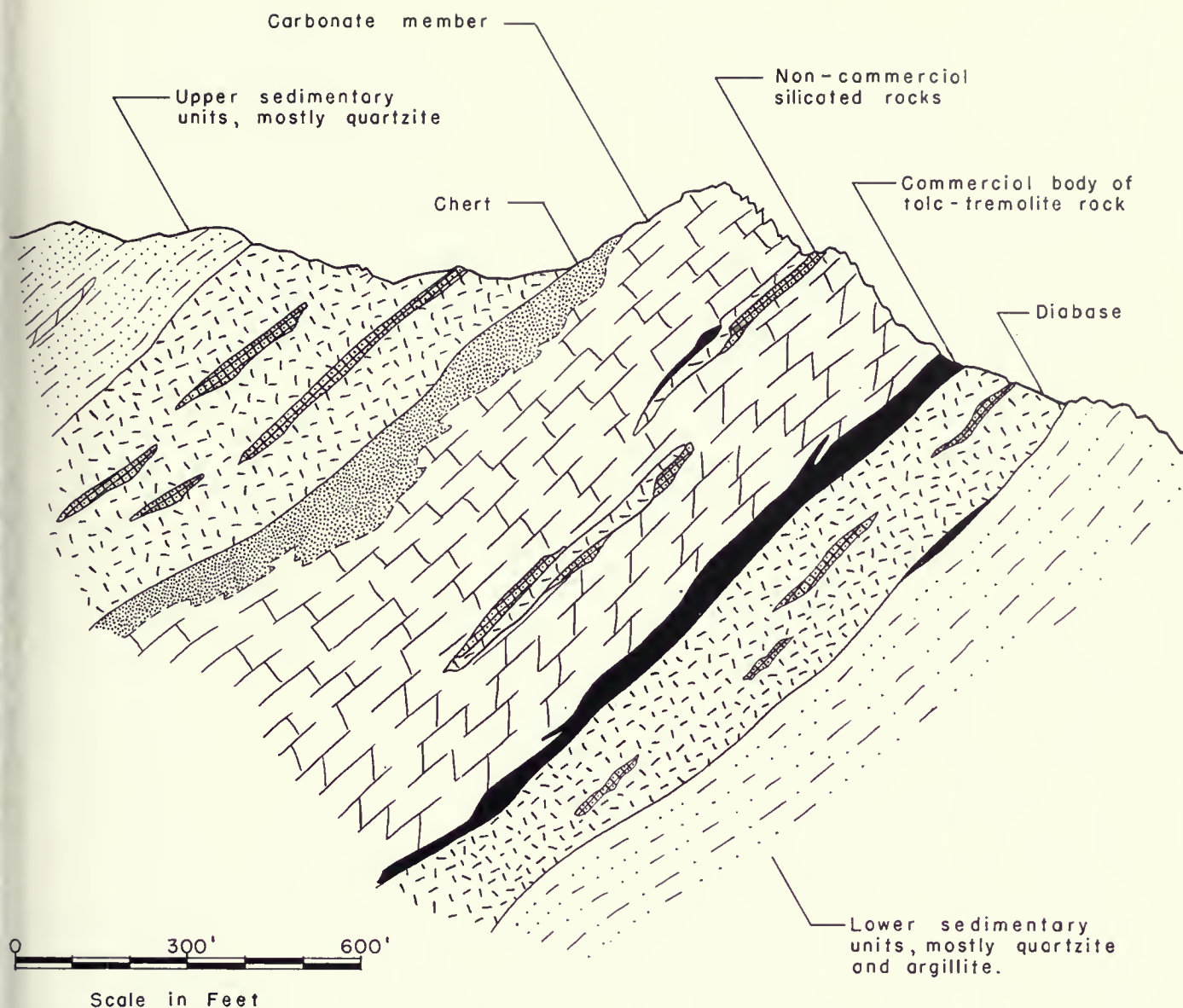


FIGURE 3. Idealized section through talc-bearing rocks typical of those in the southern Death Valley-Kingston Range region. All rock units belong to the later pre-Cambrian Crystal Spring formation.

from Vermont southward to North Carolina, in Washington, and in northern and central California. They generally are of the soapstone variety.

The alteration of carbonate strata to talc has occurred in various geologic environments. Many of the larger deposits of this type exist in regionally metamorphosed terranes in which the mineral talc has formed at a late stage of lowered temperature. In such deposits the talc commonly has replaced tremolite which developed during an intermediate stage in the alteration. Deposits of this type occur in the Gouverneur district of northern New York State and in the Silver Lake-Yucca Grove area of San Bernardino County, California.

Other talc deposits have formed as alterations of relatively unmetamorphosed carbonate strata and contain little or no material composed of other magnesium silicate materials. In California, most of the deposits of steatite-grade talc, which occur in or near the Inyo

Mountains of central and northern Inyo County, are of this type. Still other deposits that have altered from carbonate strata occur as contact-metamorphic bodies along or near the margins of diabase sills or dikes. Very large talc-tremolite bodies of this type occur in the southern Death Valley and Kingston Range region of California.

The alteration of limestone, dolomite, quartzite or granitic rocks to talc involves enrichment in magnesium, but the manner in which such enrichment takes place is not everywhere clear. Many of the deposits appear to have derived magnesia from nearby high-magnesium sedimentary rocks. Other possible sources of magnesia for some of the deposits are magmas of acidic to basic composition and groundwater that existed in the original sedimentary rocks. Magnesia enrichment in some deposits may have occurred by the removal of CaO and CO<sub>2</sub> from dolomite. The silica necessary to form the magnesium silicate minerals, in many places, appears to have been a constituent





- |                                  |                                  |                                  |                         |                              |
|----------------------------------|----------------------------------|----------------------------------|-------------------------|------------------------------|
| 1. Long Horn mine                | 7. Doris Dee prospect            | 14. Bonham (White Mountain) mine | 20. Powderpuff prospect | 27. Frisco mine              |
| 2. Nikolaus (Eureka Valley) mine | 8. Gray Eagle (Rogers, Eleanor)  | 15. Alberto and Florence mines   | 21. Lakeview mine       | 28. Talc City mine           |
| 3. Blue Star mine                | 9. Hilderman mine                | 16. Moss mine                    | 22. Eclipse mine        | 29. Gab Cat prospects        |
| 4. Blue Stone mine               | 10. Homestake prospect           | 17. Branson prospect             | 23. White Swan mine     | 30. Silver Dollar mine       |
| 5. Willow Creek mine             | 11. Ubehebe (Stone pencil) mine  | 18. Skinner mine                 | 24. Smith mine          | 31. Alliance and Irish mines |
| 6. White Eagle mine              | 12. White Horse mine             | 19. Lenbeck mine                 | 25. Viking mine         | 32. Victory mine             |
|                                  | 13. Gold Bell (Quackenbush) mine |                                  | 26. Trinity mine        |                              |

FIGURE 4. Map of the Inyo Mountains-northern Panamint Range region showing the distribution of the principal rock units and the location of talc mines and prospects. Geology modified from the Death Valley and Bakersfield sheets of the State Geologic Map, California Div. Mines, 1955, and from the original sources as shown on these sheets.



of the original rock; in other places it appears to have been introduced hydrothermally.

*Deposits of the Southern Death Valley-Kingston Range Region, Inyo and San Bernardino Counties.* About two-thirds of the annual output of talc in California is obtained from the region that extends from the southern part of Death Valley eastward to the Kingston Range, and lies in both Inyo and San Bernardino Counties (fig. 2). Here talc is confined to the Crystal Spring formation which is the lowest of the three formations that comprise the Pahrump series of later pre-Cambrian age. In its typical development this formation is about 4,000 feet thick and consists of mildly metamorphosed sedimentary rocks intruded by diabase sills (fig. 3).

The lower 1,000 feet of the formation is composed of quartzite and argillite. A carbonate member, which ordinarily consists mostly of dolomite and commonly is cherty, occupies a several-hundred-foot thickness near the center of the formation and is overlain by an additional several hundred feet of both carbonate and non-carbonate strata. Most of the diabase is confined to sills that lie immediately below or immediately above the carbonate member. The lower sill appears to be a continuous body throughout this talc-bearing region and is the one that is associated with all of the talc bodies of proved commercial interest.

These talc bodies are alterations of the lowest strata in the carbonate member and most of them are in contact with and above the diabase sill. Some exist as septa within the sill, others lie below the sill, and still others lie above the sill, but are separated from it by non-carbonate strata.

Silication is shown along nearly all of the contacts between the lower parts of the carbonate member and the lower sill, but bodies of commercial talc that can be easily mined are less widespread. In some places, the silication has been too weak to produce deposits of commercial interest; in other places the talc bodies are too thoroughly faulted to be economically mined. At about 20 localities, however, active mining operations have developed bodies of commercial talc that are essentially intact and range from 500 to 5,000 feet long and from 10 to nearly 100 feet wide. Such deposits occur in the Warm Spring Canyon-Galena Canyon area of the southeastern part of the Panamint Range, in the Saratoga and Ibex Hills, low on the north flank of the Avawatz Mountains, in the Alexander Hills, and in the Kingston Range. Inactive talc mines and prospects occur in the northern part of the Owlshhead Mountains, in the Silurian Hills and in the southern Amargosa Valley.

Although the mineralogic composition of the commercial talc differs from deposit to deposit and from place to place within individual deposits, all of the deposits contain unusually white, fine-grained material whose iron oxide content consistently is less than one percent and whose carbonate content (dolomite and calcite) ordinarily lies in the range of 3 to 10 percent. The magnesium silicate minerals consist of talc, tremolite and subordinate serpentine and are mixed in various proportions. Commonly, talc or tremolite predominates to the virtual exclusion of the other. A thinly laminated talc-rich or tremolite-rich rock occupies the lower half of many of the deposits that lie above the diabase. Else-

where, the commercial talc ranges from schistose and friable to blocky and tough. A reddish alteration rock, rich in sericite, quartz, and alkali feldspar, commonly occurs as elongate masses within the deposits or bordering them.

The largest individual body that has been developed to date is at the Western mine in the Alexander Hills. It is about 5,000 feet in exposed length, 10 to 80 feet wide, and has been explored down-dip for about 350 feet. The talc-bearing zone in the Warm Spring Canyon area appears to be even larger, but has been cut by cross-faults into several en echelon bodies. Other operations where deposits of commercial talc are continuous through distances of 1,000 or more feet are the Death Valley mine in Galena Canyon of the Panamint Range; the Eclipse mine in the Ibex Hills; the Excelsior mine in the northeast part of the Kingston Range; the Sheep Creek mine low on the north slope of the Avawatz Mountains; and the Superior mine in the Alexander Hills. Deposits of less lateral extent, but which have supported continuing mining operations, exist at the Ibex and Monarch mines in the Ibex Hills, the Pongo mine in the Saratoga Hills, the Acme and Booth mines in the Alexander Hills, and the Smith mine in the Kingston Range.

*Deposits of the Inyo Mountains—Northern Panamint Range Region, Inyo County.* Nearly all of the talc of steatite grade and much of the non-steatite talc that have been produced in California have been obtained from a region in central Inyo County that embraces the Inyo Mountains and the northern part of the Panamint Range (fig. 4). The talc deposits of this region have altered from Paleozoic sedimentary rocks and locally from Mesozoic granitic rock. These deposits, which generally are smaller and more irregular than those of the southern Death Valley-Kingston Range region, have formed mainly along fractured and sheared zones in dolomite of the Lower Ordovician Pogonip formation, the Middle Ordovician Eureka quartzite, the Upper Ordovician Ely Springs dolomite, and dolomite and quartzite of Silurian age.

Talcose zones (fig. 5) are most abundant along major contacts, especially those between quartzite and dolomite, and the talc ordinarily has replaced both rocks. The deposits that have replaced granitic rock occur in areas where these other types also exist. Many of the deposits are closely associated with bodies of a punky, limy rock which originally was dolomite and from which most or all of the magnesia, added to form the talc, appears to have been derived.

The mined material ranges in color from dark gray through pale green to white, is fine-grained, and consists predominantly of the mineral talc. Indeed the chemical composition of much of the material, when selectively mined and sorted, approaches that of the pure mineral. The principal impurities are carbonates (mainly as fracture-fillings) and iron oxides. These are abundant enough to cause much of the mined talc to be of sub-steatite grade. As much of the darker colored talc from this region fires nearly white, a dark color is not necessarily an objectionable property.

The largest and most continuously active talc mining operation in this region is the Talc City mine (fig. 6) in low hills at the southern end of the Inyo Mountains. This mine has yielded talc mainly from three bodies, two of



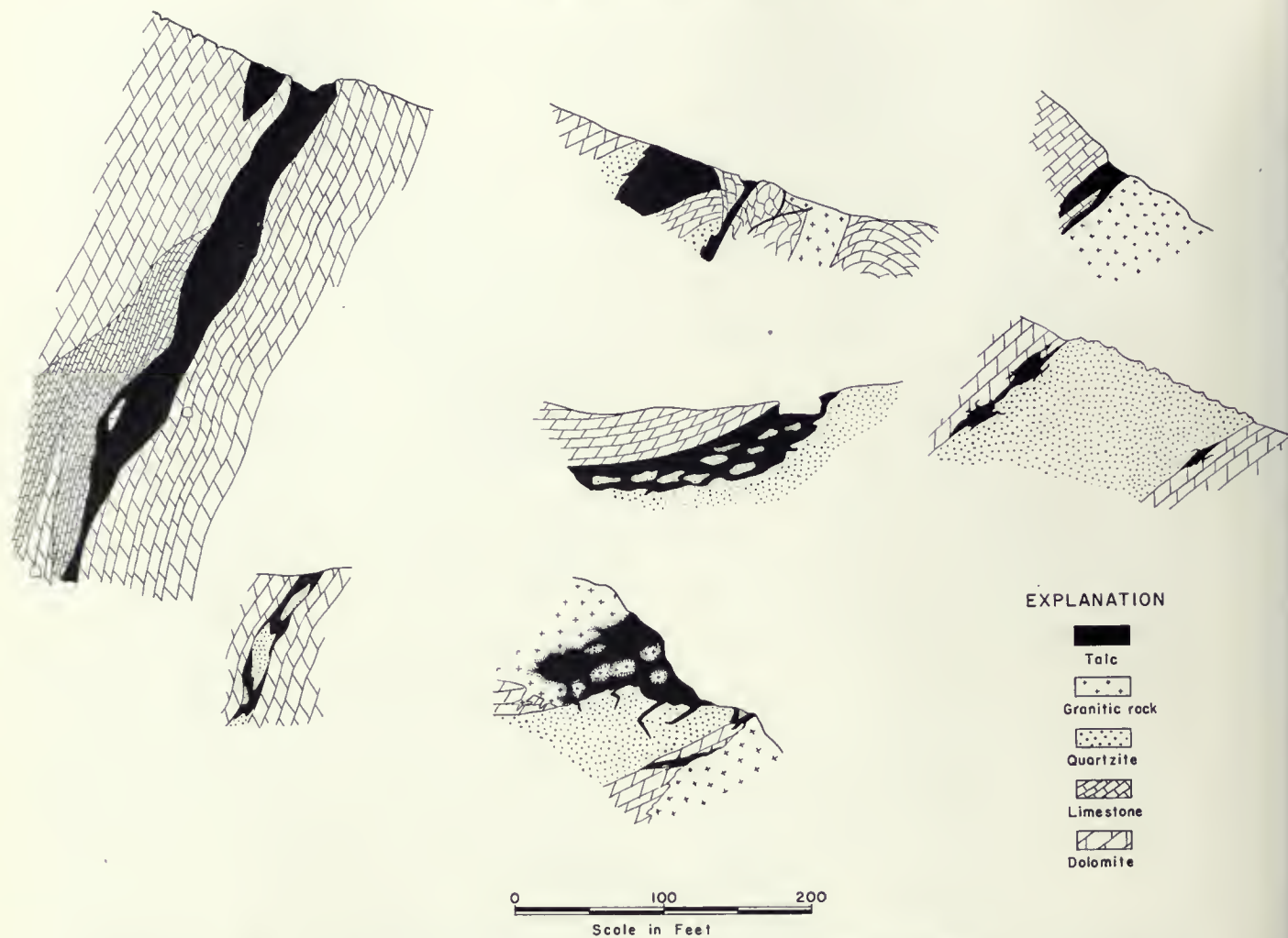


FIGURE 5. Idealized sections through talc deposits typical of those in the Inyo Mountains. Much of the talc that occurs in this manner is of steatite grade. Modified in part after Page, 1951.



FIGURE 6. Photo of Talc City mine, Inyo County, the principal source of steatite-grade talc in California. Deposits are in highly deformed carbonate strata of Ordovician age.





FIGURE 7. Photo of part of the east slope of the Inyo Mountains, showing some of the numerous shallow workings that comprise the White Mountain talc mine. These workings have developed discontinuous and irregular deposits, which consist largely of steatite-grade talc and which occur in carbonate rocks and quartzite of Silurian age. Upper Paleozoic rocks are exposed in the cliff behind the mine.

which are elongate, steeply dipping lenses, each 500 to 1,000 feet long and 50 feet in maximum width. The Tale City deposits are enclosed mainly in dolomitic limestone of Ordovician age. One of the lenses has been mined down-dip to a maximum of about 450 feet; the other apparently is much shallower. The second most productive talc-bearing area in the Inyo Mountains comprises a 2-mile belt in the southeast part of the mountains. The deposits have been developed by a group of small workings known collectively as the Bonham operations and embracing three principal mines, the White Mountain (fig. 7), Florence and Alberta. The Bonham deposits individually are smaller but much more numerous than those at the Tale City mine, and are largely or wholly replacements of dolomite and quartzite of Silurian age (C. W. Merriam, personal communication, 1951).

The rest of the talc output of the Inyo Mountains—northern Panamint Range region has been obtained mostly from the Alliance mine in the Tale City area, and the Nicolaus (Eureka) and White Eagle mine in the northeastern and east slope of the Inyo Mountains respectively. In California, only the White Eagle deposit has yielded large tonnages of talc that has altered from granitic rock. Relatively undeveloped deposits that appear to have substantial reserves exist at the Gray Eagle mine, on the west face of the Inyo Mountains and at the Ubehebe mine in the northern Panamint Range.

The massive chlorite, noted above, is obtained from the Frisco mine which is near the Tale City mine and has a similar geologic setting. The chlorite has altered from

acidic or intermediate dikes and is associated with talc that has altered from dolomite.

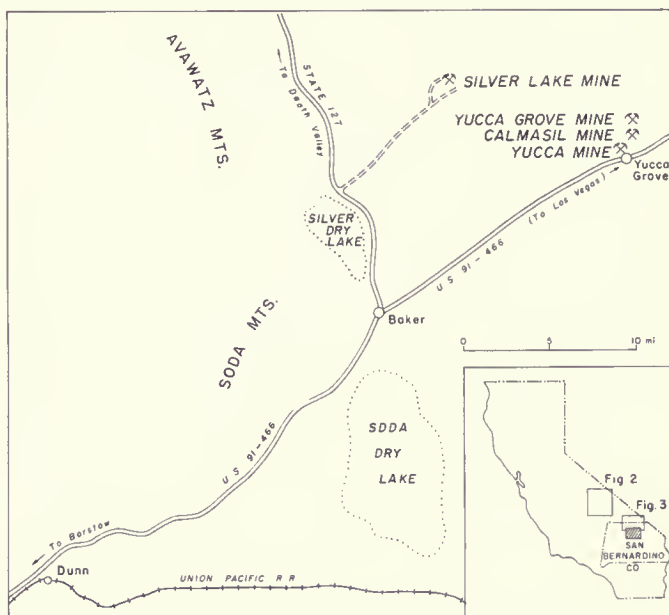


FIGURE 8. Index map showing the talc mines of the Silver Lake-Yucca Grove area and Dunn Siding, the shipping point for most of the talc mined in southern Inyo County and San Bernardino County. Relationship of this area to the areas of figures 2 and 3 is shown in inset.



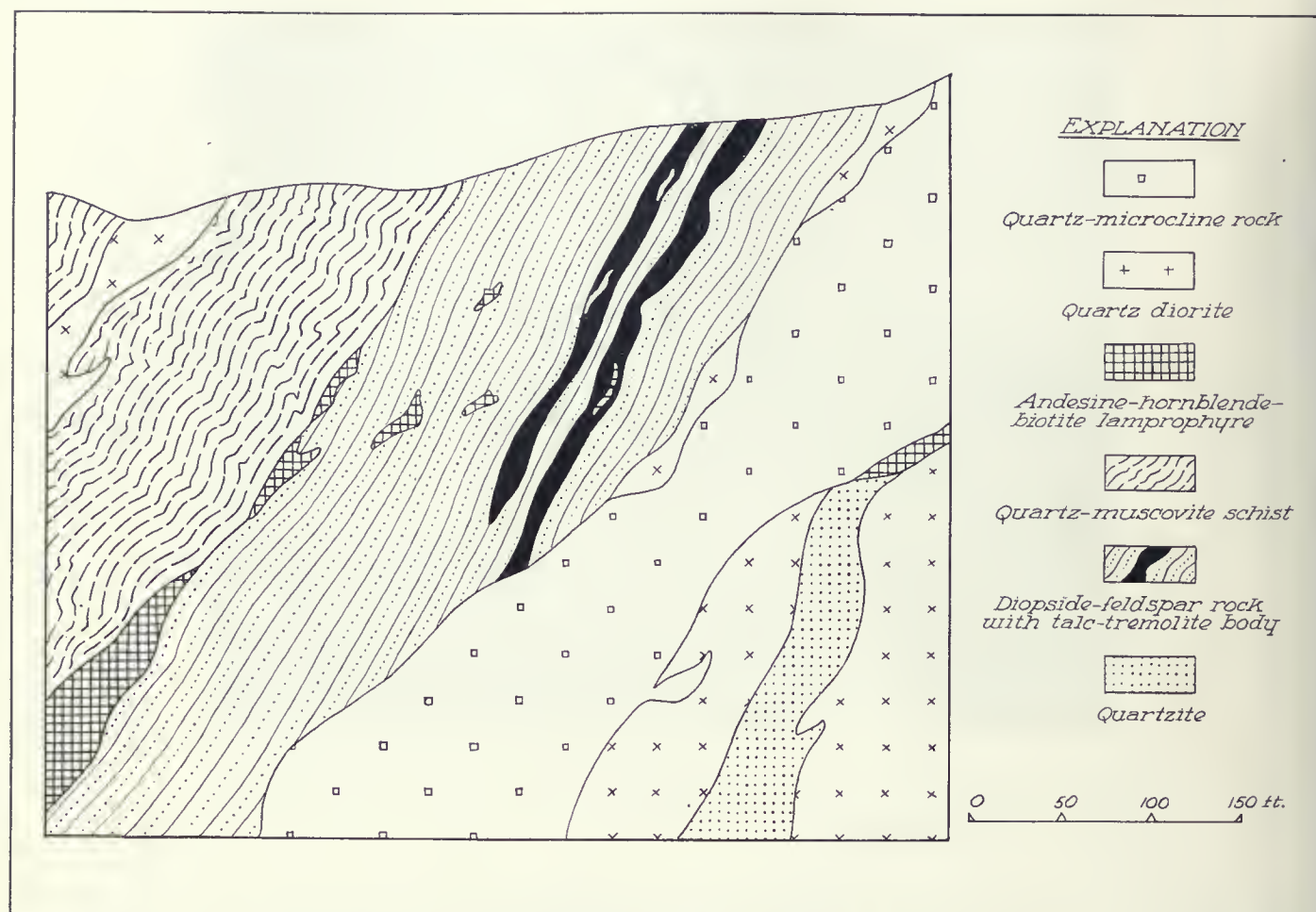


FIGURE 9. Idealized cross-section through Silver Lake talc-bearing area, San Bernardino County.

*Deposits of the Silver Lake—Yucca Grove Area, San Bernardino County.* A 12-mile belt (fig. 8) that extends eastward from the vicinity of the Silver Lake playa to the settlement of Yucca Grove in northeastern San Bernardino County, contains talc deposits that contrast markedly with those in the districts noted above. These more southerly deposits (fig. 9) occur as lenses in a terrane composed mainly of early (?) pre-Cambrian metasedimentary and intrusive rocks (Wright, 1954). They appear to be selective replacements of certain dolomitic strata and show a complex metamorphism that involved an early and nearly complete tremolitization probably concurrent with the emplacement of large bodies of granitic rock. The tremolite rock ordinarily shows a decussate texture. Concentrations of mineral talc developed later and mostly in the form of schistose masses along the margins of the tremolite bodies. Most of the talc schist and the tremolitic rock are snowy white and medium-to coarse-grained. Forsterite grains and serpentine veinlets are abundant in a darker phase of the tremolitic rock.

Most of the talc mined in the Silver Lake-Yucca Grove area has been obtained from a group of workings known collectively as the Silver Lake mine (Wright, 1954) and discontinuously distributed along a 2-mile zone. Within this zone the mineable talc bodies show an average

thickness of about 10 feet and range in length from a few tens of feet to as much as 800 feet. Most of the mine workings have encountered two parallel bodies about 15 feet apart and enclosed in feldspar-diopside-quartz-calcite hornfels. The deepest workings are on the longest of the exposed bodies and extend down-dip for about 260 feet to a level where the body appears to terminate against granitic rock.

Deposits similar to those at the Silver Lake mine occur at the Yucca Grove, Calmasil, and Yucca mines near Yucca Grove, but have been less extensively worked.

*Deposits of the Sierran Foothill Belt.* Numerous deposits of soapstone are associated with the serpentine bodies of the western foothills of the Sierra Nevada (see serpentine map in chromite section of this volume). As the deposits are alterations of the serpentine, they generally retain several percent iron which causes the soapstone to grind and fire to darker colors than do the higher-quality, essentially iron-free tales. Individual deposits rarely are more than 50 feet in width and 400 feet long, but together they constitute a soapstone reserve of many millions of tons that can be mined by surface methods. Only a very small proportion of the deposits has been developed, as the demand for soapstone has been limited and has been met by operations generally no more than 5 miles away from rail facilities.



Such deposits have contributed several hundred to several thousand tons of soapstone annually for many years and had a combined recorded output of about 90,000 tons through 1955. Nearness to markets and inexpensive mining have favored their development.

Since 1895, soapstone production has been recorded from 17 properties in seven Sierran foothill counties. Previously, soapstone had been mined in this area and used as dimension stone, but specific data on this earlier production are not available. Most operations were small, and few continued for periods greater than 10 years. The longer-lived operations include the McLean mine in Butte County and three operations in El Dorado County—the Swift mine and the Pacific Minerals mine, both near Latrobe; and the Prouty mine near Shingle Springs. Only the Pacific Minerals Company mine has been continuously active in recent years.

Other soapstone properties that have been active at one time or another since 1925, include one in Butte County, two in Calaveras County, three in El Dorado County, one in Tulare County, two in Tuolumne County, and five in Amador County.

**Miscellaneous Deposits.** Talcose material has also been produced from several other deposits scattered throughout the state. Talc deposits on Santa Catalina Island, which were worked in the eighteen-nineties, are among the first for which there is a recorded output. Since 1917, soapstone has been mined intermittently from the Katz deposit near Acton, Los Angeles County. Since 1940 small tonnages of steatite-grade talc have been obtained from the Ganim mine, a gold property near Schilling, Shasta County. The talc bodies at the Ganim mine are in an altered zone in meta-andesite.

**Mining Methods.** The talc mines of California are largely underground operations, although most of the soapstone production, as well as a small proportion of the talc output from the eastern belt, has been obtained by surface methods. In common practice, ordinary blasting techniques are used and the deposits are developed first by shallow drift-adits and then by inclined shafts sunk along or near the talc body. Drifts, spaced at 50-foot to 100-foot intervals along the shafts, follow the talc bodies. The drifts are joined by raises which are enlarged into stopes. The pillars are left large in "heavy ground." The talc is fed by gravity, commonly with the aid of slushers and jackhammers with spade bits, into ore cars which generally are trammed by hand. In some of the larger mines mucking machines are employed in driving the level workings.

In 1955, diesel rock-moving equipment was introduced at the principal workings of the Grantham (Warm Spring) mine which formerly had been developed by conventional methods. By means of a Michigan shovel loader, the talc is placed on a Koehring Dumptor truck and hauled to the surface through a 10° inclined shaft. To accommodate the two diesel engines underground, a high-capacity ventilating system was installed.

Some deposits have required little timbering, but at others, especially those that are wide and contain abundant talc schist along irregular hanging walls, timbering has been a major expense. Square-set timbering has been used at several mines with unusually large stopes. Roof-

bolting techniques have been employed increasingly in recent years.

**Treatment.** In California, as elsewhere, most talc is prepared for market by means of a preliminary crushing in jaw or rotary crushers and then grinding in roller mills in closed circuit with air separators (fig. 10). This procedure yields talc as finely ground as 99.9 percent through 325 mesh. Some mills also are equipped with fluid energy grinding mills, known as micronizers, which produce particle sizes in the range of 20 to less than 5 microns. In such mills comminution is produced by the means of mutual bombardment of talc particles under the pressure of jets of air or steam.

Very little, if any, block talc from California is now machined on a commercial basis, although in recent years small quantities of marking crayons have been made from talc mined in Los Angeles County. Although commercial talcs have proved amenable to beneficiation, the wide variety and availability of talc in California has made such practices unnecessary here.

**Utilization.** Of the 118,288 tons of talc and soapstone that were mined in California in 1953, about 65 percent was used as a ceramic raw material and about 15 percent as a paint extender. In recent years from 1,000 to 5,000 tons of California talc has been consumed annually in each of the following additional applications: filler, lubricating and calendering agent in paper manufacture, filler and lubricant in rubber manufacture, polishing and coating agent in the preparation of rice, sizing for textiles, an ingredient in toilet and pharma-

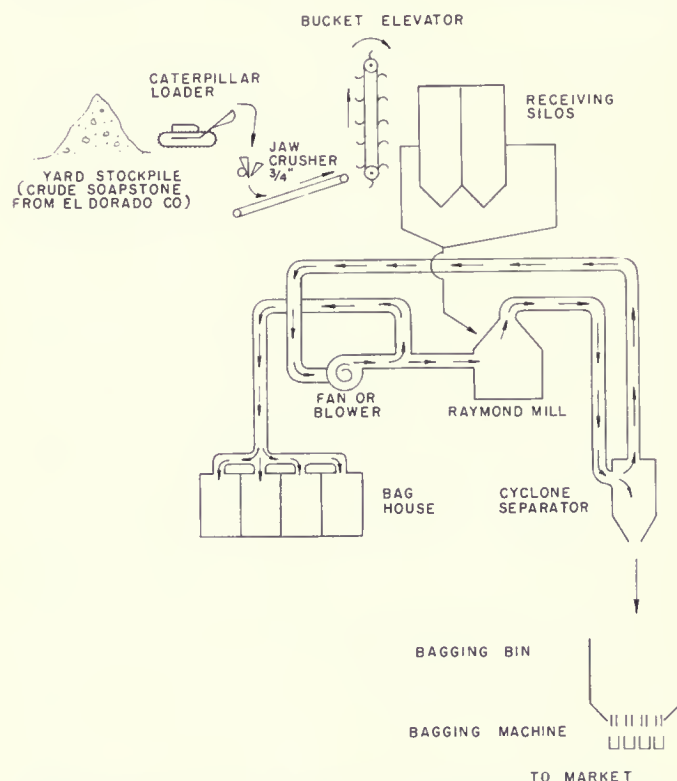


FIGURE 10. Flow sheet of a typical talc grinding mill. The bag house material either is bagged and sold separately, or is fed back into the circuit to become part of a finely ground commercial talc.



ceutical preparations, filler in asphalt, and an insecticide carrier. Smaller tonnages are consumed in many minor uses.\*

The ceramic industry requires tales that form well when the bodies are cast or pressed, that are uniform enough to assure a continuing uniformity in the dimensions of the finished products, and that fire white or nearly so. In wall tile manufacture, the principal ceramic use, mixtures containing 60 to 75 percent talc and 40 to 25 percent clay are ordinarily employed in California plants. The mixture is moistened, pressed into bisques, and fired in the range of 2100° F. to 2200° F. The dimensions of the finished tile must conform closely to standard size specification. Most 4½-inch by 4½-inch flat tile, for example, must fire within the 4.240-inch to 4.255-inch range. Before the mid-1930's wall tile bodies contained mostly feldspar and clay, but the use of talc in place of feldspar has become widespread. This practice has virtually eliminated the delayed development of minute cracks known as crazing.

Most of the wall tile manufacturers in California prefer talc with a high tremolite content and all require tales that are free of discoloring impurities such as iron oxides and manganese oxides that produce dark spots on the finished bodies and in the glaze. The tremolite is said to prevent a spalling which commonly develops during the firing of tremolite-free bisques. Several percent of carbonate material is tolerated. In California, the tales used in wall tile manufacture are obtained in the southern Death Valley-Kingston Range region and Silver Lake-Yucca Grove area. These are rather coarsely ground so that 92 to 98 percent passes through a 200-mesh screen.

The talc-rich raw material used in the manufacture of electrical insulators contains 70 to 90 percent of steatite-grade talc; the remainder consists of clay and small increments of alkaline earth oxides or carbonates and a gum. The insulator bodies, which are of many shapes and sizes are pressed or extruded and fired at temperatures in the range of 2250° F. to 2450° F.

Whether or not a talc is of steatite grade is determined when it is accepted or rejected by insulator manufacturers, but most non-steatite talc can be recognized by obvious impurities. Some talc, however, which appears similar to steatite and is of steatite purity, is not accepted for insulator manufacture because it fires off-color, or off-size, or has improper forming properties. Much of this near-steatite talc could be used as insulator material in an emergency, either straight or blended with talc of established steatite grade. As noted above, most of the talc of steatite or near-steatite grade that has been mined in California has been obtained from the Inyo Mountains region for insulator manufacture. It is ground to permit 99.5 to 99.7 percent to pass through a 200-mesh screen.

Although insulators manufactured from ground talc generally have replaced the bodies machined from block steatite, small quantities of block steatite are still required in the manufacture of spacers for power vacuum tubes. This is obtained from foreign sources as no suitable domestic sources are known, and operators state

that the steatite deposits in California are too highly fractured to yield block steatite on a commercial basis. Recent experiments in the development of built up block steatite, utilizing ground steatite and a phosphate (Comeforo, et al., 1954) or magnesium oxychloride bonding agent (Hamlin and Klinefelter, 1956), and in the development of phosphate-bonded synthetic mica products (Comeforo, et al., 1953), may provide adequate substitutes for block steatite.

Several varieties of the commercial talc mined in California are marketed for use as paint extenders. These are mainly materials from the southern Death Valley-Kingston Range region that range from tremolite-poor to tremolite-rich and contain several percent of carbonate material, but they also include talc of steatite or near-steatite grade from the Inyo Mountains region. All paint tales must grind white or nearly so. Particle shape and fineness of grinding also are important factors in fitting a talc to a type of paint.

Talc is a desirable paint extender largely for the following reasons: (1) it causes a low settling rate in the mixed paint, (2) its micaceous and acicular particles promote durability, (3) it permits the paint to flow readily and smoothly, and (4) it aids in the dispersion of pigments (Lamar, 1952). Commercial tales from the southern Death Valley-Kingston Range region, when ground to 99 percent minus 325 mesh, are used in outside house paints with a linseed oil base. The same tales ground to minus 15 microns or finer, are used in industrial enamels in order to control gloss. Similarly ground tales of steatite or near-steatite grade are used in emulsion paints.

The California tales that are used by the paper industry are of the steatite or near-steatite varieties. When ground to 99 percent minus 325 mesh, they are as a lubricating and calendering agent for high-quality paper and are applied as the paper is passed through highly polished steel rollers. When ground to 99 percent minus 5 microns, they are employed as ingredients to give opacity and brightness to the highest-quality paper.

The rubber industry uses talc mostly as a lubricant which is applied either as dry powder or in a water suspension. For this use off-color tales from the Inyo Mountains region, that otherwise resemble talc of steatite grade, are generally ground to 99.5 minus 200 mesh.

In the preparation of rice, talc of near-steatite grade which is ground to 99 percent minus 325 mesh, is (1) used as a polish to remove the outer hull from the rice grain and (2) mixed with starch to provide a coating for the grain. The textile industry employs similarly ground but lower quality talc as a sizing in cotton fabrics. For this use white talc with a minimum of abrasive constituents is desired.

Face powders and pharmaceuticals require light-colored, chemically pure talc of the highest quality. For face powder it must have uniform color tinting strength. Grinds for these uses range from 96 percent through 200 mesh to 99.9 percent through 325 mesh.

In California, the tales used as asphalt filler and insecticide carriers are mostly of the soapstone type, as off-color material is acceptable for such use, and low-cost open-pit mining permits competition with other comparably priced fillers and carriers. For these uses the

\* The above usage data were supplied by Mr. R. B. Maurer, Chief, Mineral Industry Division, Region III, U.S. Bureau of Mines. Much of the following data on specifications was obtained from R. S. Lamar, Director of Research, Sierra Talc and Clay Company.



soapstone is ground to sizes in the range of 92 to 95 percent through 325 mesh.

Steatite-grade block talc is not produced in California, but insulator bodies have been machined in the past, talc crayons have been manufactured from time to time, and talc dimension stone and refractory brick also have been quarried and finished in the state.

**Marketing.** Most of the talc mines in California are operated by concerns which also operate mills and which market ground and bagged talc either directly to consumers or by means of jobbers. Very little crude talc is sold to the ultimate consumers as they generally have no grinding facilities. The independent owner of a talc deposit is faced with several alternatives: to mine and attempt to sell the crude material to concerns with milling facilities and an outlet for the ground material; to lease or sell his deposit to such concerns; to have the talc custom milled and attempt to market the ground product; or to purchase or construct his own mill. The two first-named practices are the most common and involve the least financial risk.

The prices paid for crude talc and soapstone at the California mines ordinarily are arrived at by negotiation between the mine operators and the concerns with milling facilities. Factors considered include the cost of transportation to the mill and the demand, as well as the quality of the talc. In 1955, California tales, exclusive of soapstone, were valued in general range of \$8 to \$15 per ton at the mines. Crude soapstone was being delivered in Los Angeles for about \$5 per ton. In 1955, the Los Angeles prices for ground and bagged tales were as follows: soapstone and other tales used mostly as fillers, \$17 to \$20 per ton; ceramic and paint tales, \$30 to \$32 per ton; steatite-grade talc, \$35 to \$40 per ton; cosmetic and pharmaceutical tales, \$35 to \$50 per ton; "micronized" tales, \$50 to \$100 per ton.

Most of the market for talc mined in California lies within the state, but many thousands of tons each year are shipped to other states and foreign countries. Most of the electrical insulator manufacturers that use California steatite are on the east coast; the talc for textile sizing is marketed mostly in the southeastern states; and paint talc from California is sold throughout the United States and Canada.

**History of Operations in California.** Soapstone for utensils and ornaments is known to have been mined by pre-historic Indians on Santa Catalina Island, Los Angeles County. As early as the mid-1800's soapstone from deposits along the western foothills of the Sierra Nevada were used by white settlers for building and ornamental stone and in the linings and foundations of furnaces. Indians also are said to have mined steatite in the White Mountain mine area and, in the late 1800's, to have sold refractory brick to the operators of the nearby Cerro Gordo mine. Previously to 1916, the recorded production of talc in California had never exceeded 2,000 tons per year and consisted mostly of low-quality materials mined in the Sierra Nevada foothills and used as a filler in rubber and roofing as well as for dimension stone.

In the period 1912-1918, however, the output rose sharply when the Talc City, Western, and Silver Lake mines in the eastern part of the state were put into operation and became the principal sources of talc in Cali-

fornia. The Talc City mine was opened as a source of raw material for machined insulator bodies when foreign sources of this type of talc were cut off during World War I. From 1916 to 1935, the state's annual talc yield was in the range of 9,000 to 20,000 tons as markets developed in the paint, cosmetic, and insulator industries. This output was obtained mainly from the three mines mentioned above, but several smaller operations, in both the Sierran foothill and eastern belts, also contributed. These included the Amargosa, Booth, and Eclipse mines in the southern Death Valley-Kingston Range region.

In the mid-1930's the use of talc as a wall tile ingredient became widespread and the value of talc in the manufacture of high-frequency electrical insulators was realized. In the decade 1933-1943, the introduction of these uses together with the increased consumption of paint and wall-tile in California, caused a marked increase in the mining activity in the eastern belt, and the production of talc in California rose from about 15,000 to 65,000 tons per year. Among the larger operations that were begun during this period were the Alliance, Florence, White Eagle and White Mountain mines in the Inyo Mountain region; the Death Valley Excelsior, Ihex, Monarch, Superior, Tecopa (Smith), and Grantham (Warm Spring) mines in the southern Death Valley-Kingston Range region; and the Calmasil and Yucca Grove mines in the Yucca Grove area.

The increase continued through World War II and into the post-war period. It was sustained during the war mainly by the demand for paint and tile in defense construction and by the need for great numbers of high-frequency insulators for military electronic equipment. Steatite was, in fact, considered a critical mineral and a government order issued in October 1942, restricted the use of steatite-grade talc to applications essential to the defense effort. These restrictions were eased in February 1943 and removed in April 1943. Government stockpiling of steatite was begun early in 1943 and was continuing in 1955.

The post-war building boom caused the talc production in California to rise to about 120,000 tons in 1951 and to "level off" at about this figure in succeeding years. To sustain this production rate, most of the existing mines have been worked steadily, and several additional mines were opened in the post-war period. These last mentioned included the Eureka mine in the Inyo Mountains, and the Bonnie, Markeley and Sheep Creek mines in the southern Death Valley area.

The Defense Production Act of 1950 recognized block steatite talc as one of the minerals eligible for exploration assistance to the extent that the Government would contribute 90 percent of the cost of approved exploration projects. By mid-1956, however, no projects of this type for block steatite had been negotiated in California.

In mid-1956, the following seven concerns were both mining and milling talc in California:

Huntley Industrial Minerals, Inc., P. O. Box 305, Bishop (operating mill at Laws and working the White Eagle mine in Inyo County);

Industrial Minerals and Chemical Company, 836 Gilman St., Berkeley (operating mills at Berkeley and Florin, and working the Bryant Ranch and Hayden soapstone deposits in El Dorado County);

Kennedy Minerals Company, 2552 E. Olympic Blvd., Los Angeles (operating mill at Los Angeles and working the Death Valley and Eclipse mines in Inyo County);



Pomona Tile Manufacturing Company, 629 N. La Brea Ave., Los Angeles (working the Harry Adams and Yucca Grove mines in San Bernardino County and using the talc at its tile plant in Pomona);

Sierra Talc and Clay Company, 1608 Huntington Dr., South Pasadena (operating mills at Los Angeles and Keeler and at Grand Island, Nebraska, and working the Frisco, Gray Eagle, Markeley, Panamint (Montgomery) and Talc City mines in Inyo County, and the Ibex, Sheep Creek, Silver Lake and Yucca mines in San Bernardino County, as well as properties in Nevada and Montana);

Southern California Minerals Company, 320 So. Mission Road, Los Angeles (operating mills at Los Angeles, Ogden, Utah, and Barratts, Montana, and working the Bonnie and Panamint mines in Inyo County and the Acme Excelsior, Pongo, and Superior mines in San Bernardino County, as well as properties in Montana); and

Western Talc Company, 1901 E. Slauson Avenue, Los Angeles (operating mills at Los Angeles and at Dunn siding on Union Pacific R. R. in San Bernardino County, and working the Western mine in San Bernardino County).

Two concerns were milling and marketing talc obtained from other sources:

American Minerals Company, 840 Mission Road, Los Angeles; and Commercial Minerals Company, 310 Irwin Street, San Francisco.

Other purchasers of crude talc included:

Desert Minerals, Inc., 840 Mission Road, Los Angeles; and Hill Brothers Chemical Company, 2159 Bay Street, Los Angeles.

In addition to the Grantham (Warm Spring) mine, which was by far the most productive single talc operation in California in 1956, several independently operated properties also were active. The Bonham mine continued to yield significant quantities of talc of steatite grade. Others included the Alliance mine in Inyo County, and B. F. J. Mines in San Bernardino County.

At many of the talc mines in California most of the easily recovered talc above the 200-foot level had been removed and some had been developed down-dip for distances of 400 to 500 feet. Although the talc reserves in the Southern Death Valley-Kingston Range area probably are measurable in millions of tons, the mining problems will be increasingly more difficult.

About 60 percent of the 1,830,000 tons of talc produced in California through 1956 has been obtained from five mines: the Talc City mine with 270,000 tons, the Western mine with 260,000 tons, the Warm Spring mine with 234,000 tons, the Silver Lake mine with 230,000 tons, and the Superior mine with 120,000 tons (all figures estimated).

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## THORIUM

By BENNIE W. TROXEL

Thorium, a radioactive element and a potential source of atomic energy, is obtained almost entirely from monazite which is also a commercial source of rare earth elements. Thorium has not been produced commercially in California, although thorium mineralization has been noted at numerous places, especially in the Mountain Pass and Rock Corral areas in San Bernardino County. Thorium also occurs in black sands in several areas in the state. These occurrences have not been productive because they are either too small or too low-grade to yield concentrates at prices competitive with monazite from current sources in Africa, Florida, and Idaho. The principal purchasers of thorium concentrates are metallurgical plants in the eastern United States. Thorium compounds are used in incandescent mantles, magnesium alloys, and in chemical, electrical, and medical products. A significant demand has not developed for thorium as a source of atomic energy, but research in this field is in progress.

**Mineralogy.** Thorium is a soft, radioactive metal with an atomic weight of 232.12 and a specific gravity of about 11.75. It is not found in the native state, but is present in at least 66 minerals (Fron del, 1956). In only six of these minerals is thorium an essential constituent; in the others, thorium is substituted for other elements. A few minerals contain enough thorium to be of economic significance, but only two minerals, monazite and thorite, have proved abundant enough to have been mined as sources of thorium. Most thorium-bearing minerals are dark-colored and occur as relatively small, disseminated grains whose radioactivity, rather than their general appearance, most readily distinguishes them from common rock-forming minerals. In its occurrence and chemical properties thorium resembles uranium, cerium, zirconium, and hafnium, and it is commonly associated with rare earth elements.

Monazite ((Ce,La,Th)PO<sub>4</sub>) is a phosphate of the rare earth elements, principally cerium and lanthanum. The thorium (ThO<sub>2</sub>) content generally ranges from 5 to 12 percent, but theoretically can be as much as 26.4 percent. The specific gravity of monazite ranges from 4.6 to 5.4, and is proportional to the thorium content. Monazite generally occurs as small, equant to tabular, yellow to reddish-brown, or brown crystals. It has a conchoidal to uneven fracture, one distinct cleavage and others less distinct, and a resinous or waxy luster.

Thorite (ThSiO<sub>4</sub>), a thorium silicate, ideally contains 81.5 percent thorium. This percentage is generally less because other elements are substituted for thorium (Fron del, 1952, p. 569). It is black to brown, has a glassy or greasy luster, hardness of 4.5 to 5, specific gravity range of 4 to 6, and a conchoidal fracture. It occurs as small prismatic crystals or is massive.

Thorianite, an oxide of thorium and uranium, has a thorium content of 45.3 to 87.9 percent. It is dark gray, brownish black, or black, has a horny to sub-metallic luster, hardness of 6.5, specific gravity of 9.7, one perfect cleavage, and an uneven to subconchoidal fracture. Its most common crystal habit is small cubes.

Several other thorium-bearing minerals are widely but sparsely distributed. Those that have been noted in California include allanite (Ca,Ce,Th)<sub>2</sub>(Al,Fe,Mg)<sub>3</sub>Si<sub>3</sub>O<sub>12</sub>(OH), betafite (U,Ca)(Nb,Ta,Ti)<sub>3</sub>O<sub>9</sub>·nH<sub>2</sub>O?, euxenite (Y,Ce,U,Ca,Fe,Pb,Th)(Nb,Ta,Ti,Sn)<sub>2</sub>O<sub>6</sub>, xenotime (YPO<sub>4</sub>), and zircon (ZrSiO<sub>4</sub>).

**Geology of Thorium Deposits.** Thorium is nearly as abundant in the earth's crust as lead and about three times as abundant as uranium, but rich deposits are rare. All but a small fraction of the thorium in the world occurs in small crystals of monazite, allanite, zircon, sphene, and apatite, which are disseminated in metamorphic and igneous rocks, including pegmatites. Quartz-poor pegmatites associated with alkalic igneous rocks generally are richer in thorium than other types (Fron del, 1956, p. 576), but pegmatites have yielded thorium only as a by-product of other mineral commodities such as feldspar, lithium, or mica. Although the thorium disseminated in this manner comprises a tremendous reserve, even the richest of these deposits are too sparse to be mined for the thorium minerals alone. Available data indicate that the thorium content of most igneous rocks is within the range of zero to 25 parts per million, but some igneous rocks contain as much as several hundred parts per million (Twenhofel and Buck, 1956, p. 562). Vein deposits of monazite and thorite are rare, but monazite veins in Africa currently yield much of the world's supply.

As monazite resists weathering and is heavy, it tends to become concentrated in placer deposits. The heavy fractions in placer deposits are richer in monazite than the igneous and metamorphic rocks from which they were derived and can be mined much easier. Placer deposits have been and continue to be the world's principal source of monazite and hence of thorium and rare earths.

Thorium-bearing igneous and metamorphic rocks of considerably higher-than-average grade have been noted in Idaho, Montana, South Dakota, Michigan, California, and in the southeastern United States. Pegmatites in which thorium is particularly abundant occur in Beaverhead County, Montana; El Paso County, Colorado; and Worcester County, Massachusetts (Twenhofel and Buck, 1956, p. 566).

Monazite-bearing igneous and metamorphic rocks of the southeastern United States have been traced along two northeast-trending belts. One belt, from 5 to 40 miles wide, extends for 600 miles through Alabama, Georgia, North and South Carolina, and Virginia. The other, about 5 miles wide, extends for 200 miles through North Carolina and Virginia and merges with the longer belt in Virginia. The principal monazite-bearing rocks are biotite-rich granite and quartz monzonite, granite gneiss, and various kinds of rock into which granitic rocks have intruded. These rocks are estimated to contain 0.00005 to 0.02 percent monazite (Mertie, 1953, p. 28). They are the source of the monazite in extensive placer deposits along these belts and along the Atlantic coastal plain.



The Idaho batholith, in central Idaho, a complex igneous rock body 300 miles long and 50 to 100 miles wide, contains monazite as the most widespread radioactive accessory mineral in certain porphyritic rocks, principally those of quartz diorite to quartz monzonite composition. The monazite is erratically distributed in the rocks, and ranges from extremely minute proportions to as much as 0.01 percent (Mackin and Schmidt, 1956, p. 588). The batholithic rocks are the sources of monazite in extensive placer deposits in Idaho.

Vein-forming thorite and monazite have been discovered in several localities in the world since World War II. Probably the most significant of these deposits is a monazite-bearing quartz vein in pre-Cambrian granitic rocks in northwestern Cape Province, Union of South Africa. The vein, which is of hydrothermal origin, locally contains as much as 70 percent monazite and 5 percent copper, ranges in width from a few inches to more than a foot, and is exposed along the surface for several hundred feet (Nininger, 1954, p. 100). In 1956, this deposit was supplying nearly all of the monazite that was being processed in the United States even though the thoria content was reported to be only 1 to 2 percent.

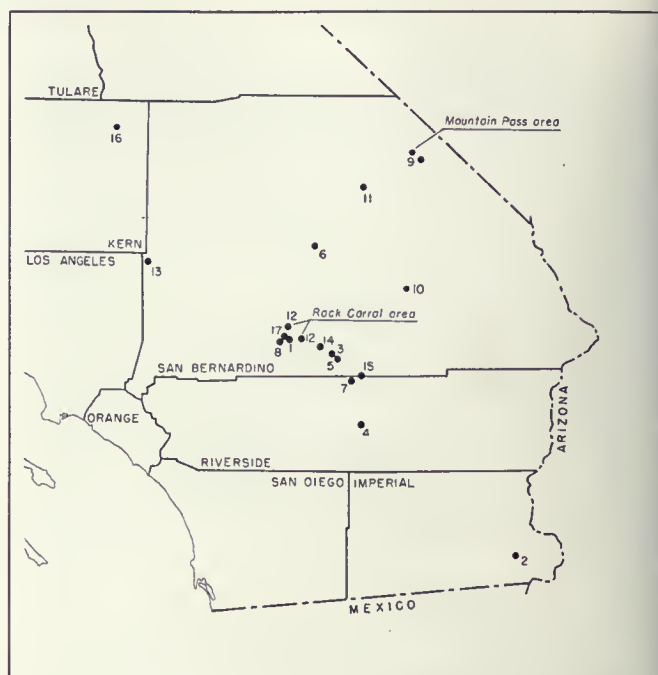
In the United States, thorium-bearing veins have been found in California, Colorado, Alaska, New Mexico, Wyoming, Montana and Idaho. Most thorium-bearing vein deposits are characterized by the association of barite, carbonates, and iron oxides and occur in igneous and metamorphic rocks that have been intruded by alkali igneous rocks. Such deposits contain from 0.1 percent to 6 percent thoria, range in thickness from a few inches to 50 feet, and in length from a few feet to 5,000 feet (Twenhofel and Buck, 1956, pp. 563-564).

Formerly, the principal foreign sources of monazite were placer deposits in Brazil, Ceylon, and India. Only a small proportion of monazite mined from these sources, however, is now exported to the United States. In most of the placer deposits monazite is recovered as a by-product of gold, zircon, cassiterite, magnetite, ilmenite, or rutile. Other minerals have been recovered in smaller quantities (see sections on black sands and titanium elsewhere in this volume). Nearly all of the productive placer deposits are of Recent geologic age.

In the United States monazite has been recovered from stream gravels and beach sands in the southeastern Atlantic states and from stream gravels in Idaho. Only the deposits in Idaho and Florida have been mined in recent years; and these have been dredging operations.

At the sites of earlier mining, in the higher parts of streams in North and South Carolina, the richer placers averaged about 8.4 pounds of monazite per cubic yard, and locally was as much as 5 times as rich (Mertie, 1953, pp. 7-12). Farther downstream and along the beaches where larger quantities of sands are available, the monazite content is less. At Jacksonville, Florida, the monazite content of the beach sand is about 0.03 percent (Mertie, 1953, p. 15).

The monazite-bearing placer deposits of Idaho are along the western edge of the Idaho batholith, and contain about two to three pounds of monazite per yard of gravel (Nininger 1954, p. 98). The monazite is recovered along with gold, ilmenite, magnetite, garnet, rutile, and in some gravels, with uranium-bearing minerals.



After Walker, Levering, and Stephens, 1956

- |                           |                              |
|---------------------------|------------------------------|
| 1. ALPHA CLAIMS           | 9. MOUNTAIN PASS AREA        |
| 2. AMERICAN GIRL MINE     | 10. ORIGINAL AND PACK SADDLE |
| 3. COPPER MOUNTAIN CLAIMS | 11. RAINBOW GROUP            |
| 4. DESERT VIEW CLAIMS     | 12. ROCK CORRAL AREA         |
| 5. HOME STRETCH GROUP     | 13. ROLL PROPERTY            |
| 6. HOERNER-ROSS PEGMATITE | 14. STEINER CLAIMS           |
| 7. LIVE OAK TANKS AREA    | 15. URANUS CLAIMS            |
| 8. LUCKY SEVEN CLAIM      | 16. WILKERSON NO. 1 CLAIM    |
|                           | 17. ZABDIEL MINING CO. CLAIM |

FIGURE 1. Thorium deposits in California. Includes pegmatite localities described in Special Report 49 (1956); placer deposits not shown.

Crawford (1956, p. 879) has tabulated the thoria content of monazite from placer deposits as follows: India, 5 to 10 percent; Brazil, 6 percent; Ceylon, 8 percent; Australia, 4 to 5 percent; Malay Peninsula,  $3\frac{1}{2}$  to 9 percent; North and South Carolina, 5 to 7 percent; Idaho,  $3\frac{1}{2}$  to 5 percent; and Florida,  $4\frac{1}{2}$  to 6 percent.

*Occurrences in California.* In California, as elsewhere, thorium minerals occur as (1) disseminations in igneous and metamorphic rocks, (including pegmatites) (2) placer concentrations, and (3) veins. Most of the occurrences of primary thorium minerals (disseminations and veins) have been noted in the Mojave Desert, principally in the Mountain Pass and Rock Corral areas of San Bernardino County (fig. 1). Low-grade thorium bearing placer deposits, largely in northwestern California, have been known for many years.

Thorium minerals disseminated in large bodies of granitic rocks, in pegmatites, and in metamorphic rocks contain most of the thorium known to exist in California, but these deposits are much too low-grade to be mined commercially under present (1956) marketing conditions. A few high-grade bodies have been discovered as pods in pegmatite dikes and as pods and veins in metamorphic rocks, but to date these have proved to be only of mineralogical interest. In California the known placer concentrations of thorium minerals are generally of



higher grade than the disseminated deposits, but they too are sub-commercial.

The Rock Corral area lies midway between Lucerne Valley and Twentynine Palms, and is near the north-west end of a thorium-bearing belt that extends along the northeastern edge of the San Bernardino Mountains (fig. 1). Detailed studies of the Rock Corral area (Moxham, Walker, and Baumgardner, 1955) have shown that here pre-Cretaceous quartz monzonite intrudes a pre-Cambrian complex of igneous and metamorphic rocks. Both the quartz monzonite and the intruded complex contain disseminated allanite and zircon. A few samples of quartz monzonite contained as much as 4.5 percent allanite and 1.5 percent zircon, but the principal mass of this rock which underlies an area of about half a square mile, has a uranium equivalent\* of only about 0.006 percent. Biotite-rich inclusions in the quartz monzonite contain higher percentages. One of these was observed to contain 0.032 percent equivalent uranium, another 7 percent allanite and 1 percent zircon. Most inclusions show areal outcrops of a few hundred square feet but they are distributed over an area of about 1½ square miles. Throughout the rest of the belt, thorium minerals have been found in pods of biotite gneiss, in pegmatite bodies and, at the Black Dog claim in the Rock Corral area, in an allanite- and monazite-bearing vein which is about 15 feet long and as much as 6 inches wide. Three samples of nearly pure monazite collected by D. F. Hewett of the U. S. Geological Survey, contained 16.10, 15.70 and 12.30 percent  $\text{ThO}_2$ . These analyses indicate that the thorium content of pure monazite from the vein is about the highest recorded in the United States (D. F. Hewett, 1956, personal communication).

In the Mountain Pass area thorium minerals occur (1) in veins and mineralized shear zones that cut pre-Cambrian gneisses, syenite, and shonkinite, (2) as disseminations in the principal rare earth-bearing carbonate body (see rare earth section elsewhere in this volume), and (3) disseminations in shonkinite, syenite, and granite. Rare earth deposits and associated thorium minerals are distributed along a belt about 6 miles long and 1½ miles wide, and have been studied in detail (Olson, Shawe, Pray and Sharp, 1954).

The veins, which are composed mostly of a mixture of carbonate minerals including bastnasite [ $(\text{Ce}, \text{La})(\text{CO}_3)\text{F}$ ], contain thorite, and, in some places, monazite. The mineralized shear zones resemble the veins, but are less well-defined, and are characterized by parallel shear planes, gouge, breccia, and veinlets of carbonate material. Analyses of thorium-rich vein material show as much as 6 percent thorium, but the average thorium content is between 0.1 and 2.39 percent. Thorite is most abundant in the shear planes that are filled with iron oxides, sericite, chlorite, quartz, and carbonates. The veins, more than 200 in number, rarely exceed 6 feet in thickness or 500 feet in length; shear zones are from 1 to 20 feet thick and are not persistent along strike. Some of the veins and shear zones might constitute commercial sources of thorite should the value of thorium increase (Olson, Shawe, Pray, and Sharp, 1954, p. 63).

Monazite occurs as disseminations in the principal rare earth deposit at Mountain Pass. This deposit is a carbonate body about 2,400 feet long and 400 feet in average width. Its thorium content ranges from 0.01 to about 0.16 percent, but locally is as high as 3 percent. The monazite constitutes a potential by-product of the rare earth operation should the future price permit its profitable recovery. Allanite occurs as disseminations in shonkinite, syenite, and granite but in an average quantity of less than 0.1 percent, which is too small to be of commercial grade.

Large concentrations of heavy minerals in placer deposits exist at many localities in California (see section on black sands elsewhere in this volume), but the sampling of these deposits to date has revealed few, if any, monazite deposits of present commercial interest. An early investigation (Day and Richards, 1905), which included the analyses of 81 samples, showed only 4 that contained 0.1 pound or more monazite per ton of sand. The highest concentration — 56 pounds per ton — was found in a sample of beach sand collected near Crescent City, Del Norte County.

*Processing.* Monazite is treated to yield high-purity thorium metal in three phases: 1) mechanical separation

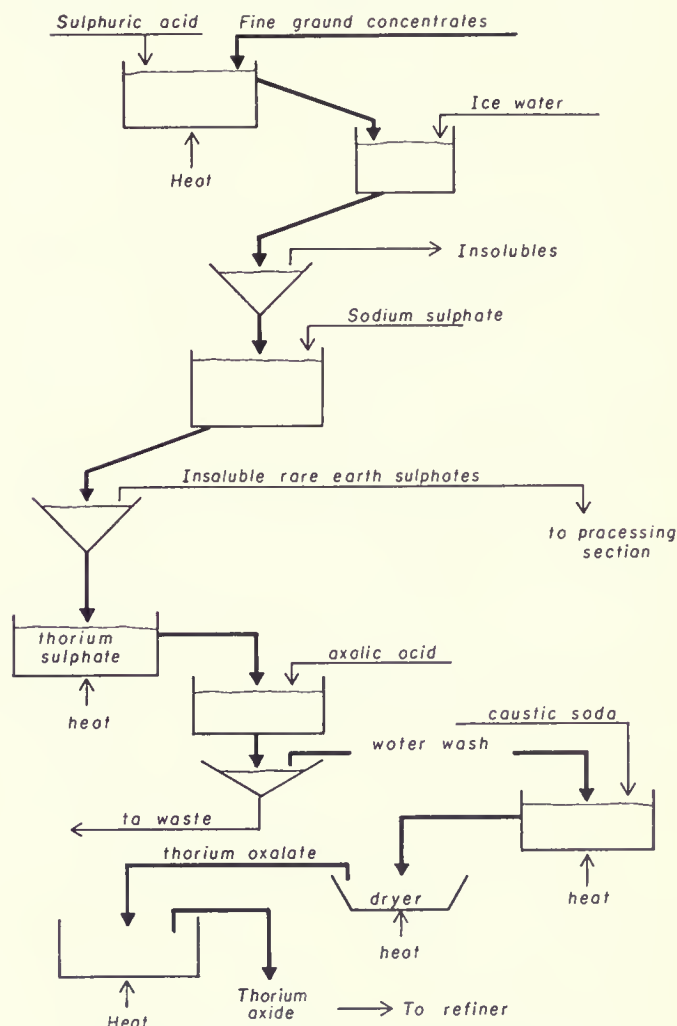


FIGURE 2. Diagrammatic flow sheet for chemical digestion of monazite.

\* Equivalent uranium is the percentage of uranium in equilibrium that will produce the observed amount of radioactivity, regardless of the source—uranium, radium, thorium, etc. Per unit weight, uranium in equilibrium is about three times as radioactive as thorium in equilibrium.



of monazite from other heavy minerals in sands, 2) chemical treatment to separate thorium oxide from rare earth oxides, and 3) thermal reduction of thorium oxide to thorium metal.

Mechanical separation is ordinarily accomplished at the site of the mining. Large deposits of black sands are mined by dredge, dragline, sluicing, or hydraulicking, and the heavy minerals are concentrated with jigs, tables, sluices, or spirals. Heavy mineral concentrates are separated magnetically and electrostatically into nearly pure concentrates of individual minerals such as monazite, rutile, garnet, magnetite, ilmenite, and zircon.

Thorium oxide and rare earth oxides are recovered from monazite by chemical digestion in either acid or caustic alkali solutions. Both processes are similar in that fine-ground monazite is decomposed in chemical solutions and undergoes several stages of filtration and precipitation that separates thorium oxide, rare earth oxides, and uranium oxide (fig. 2).

In the most common method of thorium metal production, thorium oxide is fed by batches into furnaces and reduced to the metal in the presence of sodium, calcium, or magnesium. In most operations the feed consists of a mixture of thorium oxide, metallic calcium flakes and calcium chloride, and the reduction takes place at about 1,100 degrees C. in the presence of an inert gas such as argon. Metallic thorium powder yielded from this thermal reduction process is compacted and sintered at 1,300 to 1,450 degrees C. to yield nearly pure metal.

*Utilization and Consumption.* Thorium is used mostly in the manufacture of incandescent mantles. It is also used in alloys of magnesium and tungsten, as a constituent in special optical glass, as a catalyst, in refractories, in electronic tubes, and in medical and dental compounds. It is a potential source of atomic energy. Table 1 shows the Atomic Energy Commission's authorizations for purchase of thorium compounds, for the principal non-energy purposes during the years 1947 to 1954. Import and consumption data are not released by the Atomic Energy Commission.

The incandescent gas mantle, which was invented in 1885 by von Welsbach, an Austrian, is impregnated with a compound composed of about 99 percent thorium nitrate and one percent cerium nitrate. The mantle becomes luminous after the nitrates have been ignited and converted to oxides. Although electric lights have largely replaced the use of gas and gasoline lights, the gas mantle industry still constitutes the principal market for non-energy purposes for thorium.

Thorium metal added to magnesium alloys imparts better mechanical properties at elevated temperatures

and improves the durability of the alloys and the stability of these properties after heating.

The electrical industry of the U. S. consumes thorium oxide in the production of tungsten filaments that have high resistance to mechanical shock. From 0.8 percent to 1.2 percent thorium oxide is incorporated in the tungsten. Colloidal thorium oxide, added to the usual "getter" in electronic tubes, facilitates final vacuum and maintenance of the vacuum during the life of the tube. Thorium metal is used in electron emission tubes and in special lamps to aid in starting the lamps (Crawford, 1956, p. 880).

Thorium compounds have several chemical and medical applications. Thorium oxide is used as a catalyst in petroleum cracking processes, in oxidizing ammonia to nitric acid, converting carbon monoxide to water gas, and in making many organic reagents. Insoluble thorium salts are used in some dental powders and pastes, and in medical preparations to cure certain parasitic skin infections. Soluble thorium salts are used in skin creams and lotions.

Although its resistance to thermal shock is poor, thorium oxide is employed as a refractory material (Lilliendahl, 1954, p. 452) because it has a high melting point (more than 2800 degrees C.) and is the most stable of the refractory oxides. It is used as an ingredient for polishing compounds. Thorium-228 can be used in dissipating static electricity, and mesothorium, a disintegration product of thorium, is added in small quantities to self-luminous paints for instrument dials (Crawford, 1956, p. 880).

When thorium-232, the naturally occurring isotope of the element, is bombarded by neutrons, it is converted into fissionable uranium-233. Thorium, therefore, might be used in atomic reactors. Experimental "breeder" reactors have been completed that theoretically create more nuclear fuel than they consume by producing uranium-233 from thorium in quantities that exceed the amount of fuel (uranium-233, uranium-235, or plutonium-239) consumed in the conversion (Crawford, 1956, pp. 880-881).

*Markets and Prices.* Since 1948, the purchase, sale or transfer of thorium ores has been controlled by the U. S. Atomic Energy Commission. Persons desiring to ship thorium-bearing material must first obtain a permit from the Atomic Energy Commission.

The principal domestic producers of thorium compounds from monazite concentrates are:

Lindsay Chemical Company, West Chicago, Illinois.  
Maywood Chemical Works, Maywood, New Jersey.  
Rare Earths, Inc., Paterson, New Jersey.

Table 1. Atomic Energy Commission authorization for purchases of thorium compounds for non-energy purposes in the United States (pounds of contained  $\text{ThO}_2$ ).\*

Industry	1947	1948	1949	1950	1951	1952	1953	1954
Magnesium alloys.....	--	--	--	--	--	--	3,600	4,647
Gas-mantle manufacture.....	26,658	36,697	44,621	48,471	31,132	25,427	8,707	9,765
Refractories and polishing compounds.....	3,110	1,634	1,847	1,889	3,382	1,157	236	24
Chemical and medical.....	1,176	1,767	596	2,097	6,246	11,064	5,179	3,738
Electrical.....	1,283	427	237	314	1,457	277	1,222	2,016
Total ( $\text{ThO}_2$ ).....	32,227	40,525	47,301	52,771	42,217	37,925	18,944	20,190

\* From Minerals Yearbook and Bulletin 556, U. S. Bureau of Mines.



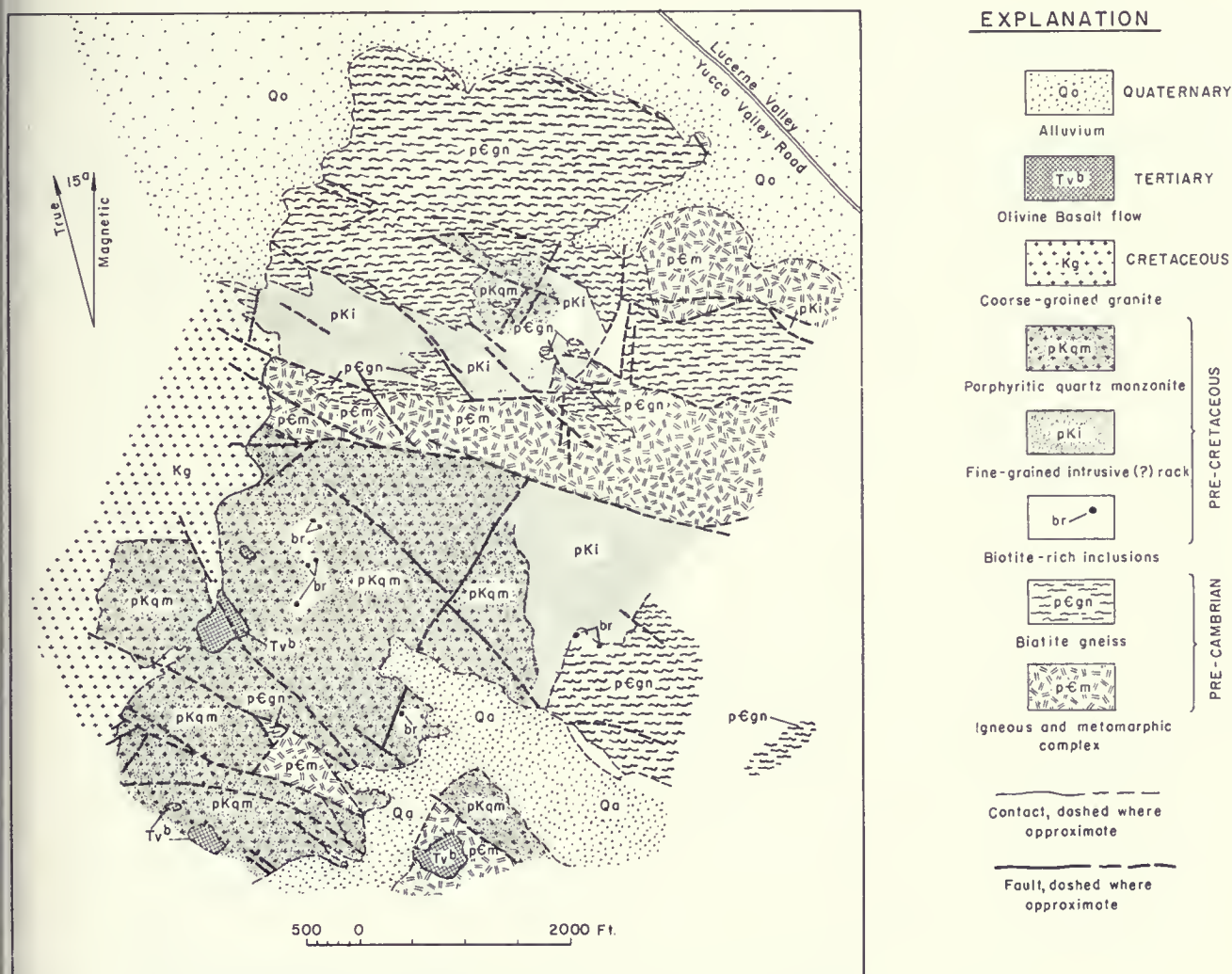
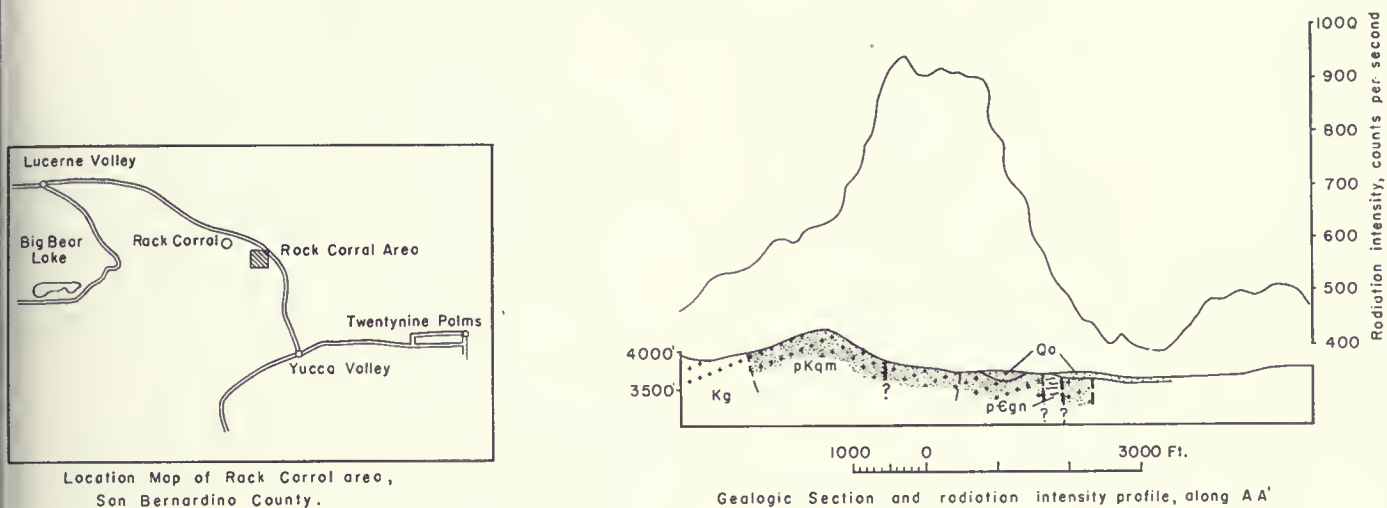


FIGURE 3. Geologic map of the Rock Corral area, San Bernardino County. The biotite-rich inclusions in the porphyritic quartz monzonite contain the most significant concentrations of radioactive minerals. Radioactivity in the porphyritic quartz monzonite is highest in the northeast part of its principal outcrop area. Generalized after Morham, Walker, and Baumgardner, 1955, pl. 15.



The monazite or other thorium ores purchased by these and other domestic producers are generally made by contract.

Prices paid for monazite ores are relatively stable, but have been gradually rising since about 1946. Market quotations ordinarily refer to the total combined rare earth oxides and thorium oxide rather than for the thorium oxide content. Some purchasers specify a minimum thorium oxide content as well. In 1955, market prices held steadily at 13 cents per pound (\$260 per short ton) for monazite containing 55 percent total rare earth oxides, including thorium, to 20 to 22 cents per pound (\$400 to \$440 per short ton) for monazite containing 68 percent total rare earth oxides (Eng. and Min. Jour. Metal and Mineral Markets). The above prices are for material delivered c. i. f. eastern seaports. The price in 1946 for monazite concentrates containing a minimum of 70 percent rare earth oxides was \$70 per ton.

In 1955, Lindsay Chemical Company was offering about \$300 per net short ton, in carloads, West Chicago, Illinois, for monazite ores containing 60 percent rare earth oxides plus thorium oxide. Thorite ores in carload lots, Colorado, had an approximate value of \$1.00 per pound of contained thorium oxide for concentrates analyzing 10 percent or more thorium oxide.

The price during 1954 for thorium metal in powder, sintered bar, and sheet form was 45, 65, and 85 cents, respectively, per gram, in less than 200 gram lots. Thorium nitrate, mantle grade, was \$3.35 per pound and thorium oxide, 99 percent  $\text{ThO}_2$  was \$9.35 per pound (Crawford, 1956, p. 880).

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# TIN

By CLIFFTON H. GRAY, JR.\*

The important place of tin in the American economy has been well demonstrated in times of peace and war. No adequate substitute has been found for its major use as a protective coating for other metals. Although the United States consumes about 40 percent of the world's tin output, the few scattered tin deposits in the continental United States and Alaska have contributed less than 0.02 percent of the world's production (Umhan, 1932, p. 13). California is among the few states with a recorded production of the metal.

## MINERALOGY AND GEOLOGIC OCCURRENCE

Cassiterite ( $\text{SnO}_2$ ), which has an adamantine luster, a high specific gravity, and is generally brown or black, is the principal tin-bearing mineral, but in a few localities tin has been recovered from lode deposits that contain stannite ( $\text{Cu}_2\text{FeSnS}_4$ ) and several other tin-bearing minerals. Tin minerals are widely distributed throughout the world, but in only a few areas are the deposits large enough to be profitably mined. Most of the world's tin supply is obtained from alluvial deposits in the Far East and in Africa. Bolivia is the only important source of tin in the western hemisphere and is the only major tin-producing country in which the tin ores occur in veins and require underground mining.

The primary tin deposits show a characteristic genetic relation to acidic igneous rocks, particularly to granite

and granite pegmatites. The Bolivian deposits are associated with quartz monzonite. Most tin veins, including those in Bolivia, are high-temperature hydrothermal deposits and are believed to have formed under high pressures deep beneath the earth's surface. Although wood tin, a nodular variety of cassiterite, occurs in rhyolite flows, prospecting for primary tin deposits is generally confined to areas in which large bodies of acidic intrusive rock are exposed.

As cassiterite is extremely resistant to alteration, it is liberated by weathering and disintegration of the enclosing rocks. Because of its high specific gravity, it is easily concentrated in placer deposits. Placer deposits in southeastern Asia, of which those in the Federated Malay States have been the most productive, are the world's principal tin sources and furnished 30 percent of the total world production in the period 1926-50 (Bateman, 1950, p. 547). Concentrations of cassiterite also occur in cluvial deposits, on the slopes immediately below the vein outcrops.

## LOCALITIES IN CALIFORNIA

Cassiterite, the only tin-bearing mineral known to occur in California, has been reported at numerous localities in the state; most of these are in its southern part (Segerstrom, 1941, pp. 549-552; Bedford and Johnson, 1946, 14 pp.). The tin occurrences in California that have been worked or have attracted attention as possible commercial sources are primary deposits. The absence of

\* Partly extracted from a section by L. A. Norman, Jr. in California Div. Mines Bull. 156.

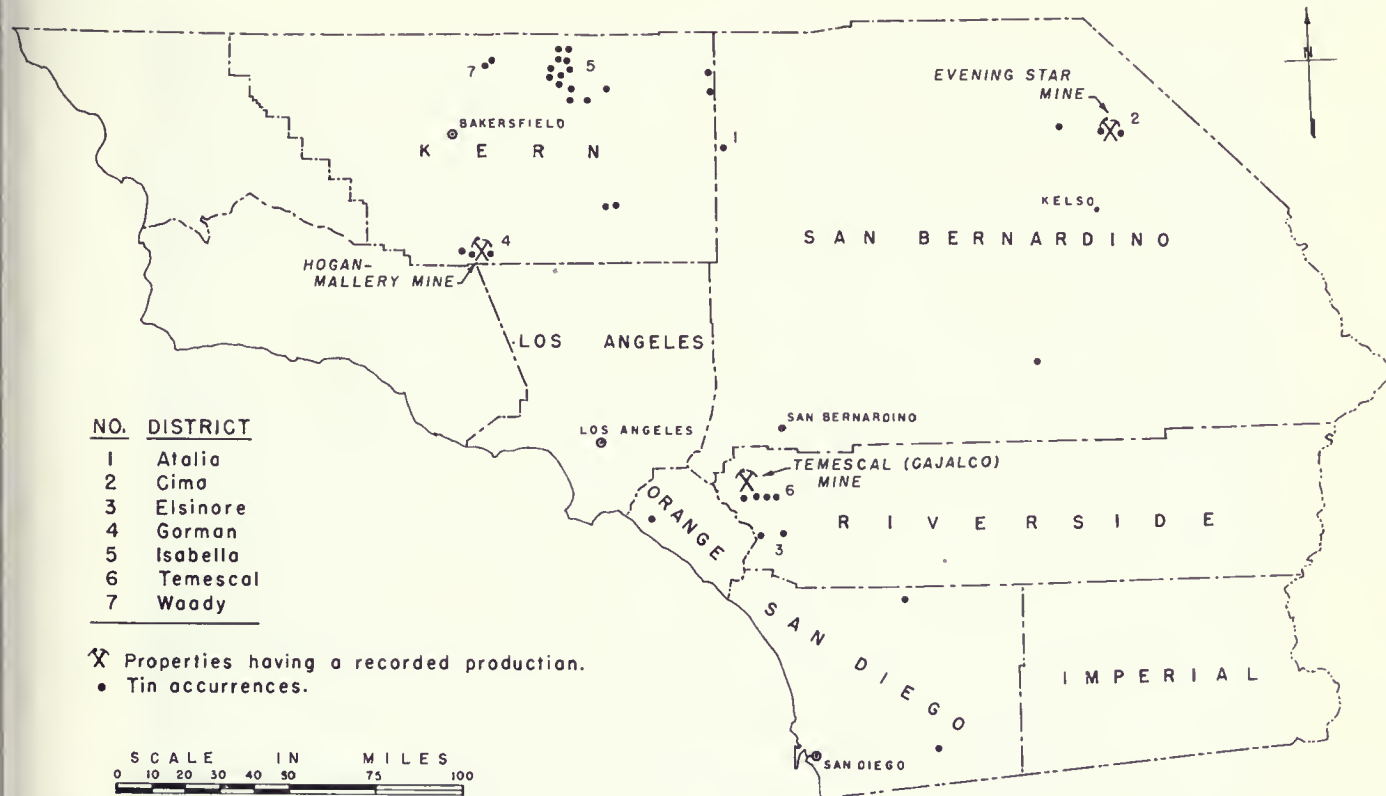


FIGURE 1. Index map showing California districts from which rocks containing more than 1 pound of tin per ton of rock sample have been reported, and properties having a recorded production of tin. Adapted from Bedford, R. H., and Johnson, F. T., 1946, fig. 1.





FIGURE 2. Temescal (Cajaleo) tin mine in 1891; view north. *Photo from historical collection of Title Insurance and Trust Company of Los Angeles.*



FIGURE 3. Temescal (Cajaleo) tin mine in 1955; view north. Cajaleo Hill in left foreground shows outcrop of mottled tourmaline-rock pipe. All buildings have been removed and only the foundations, tailing piles, and caved shafts mark the site. *Photo by Horace Parker, Bolboa Island, California.*



known concentrations of placer tin in California points against the former or present existence of large vein deposits exposed at the surface.

Three mines in the state have recorded productions of tin. These are the Temescal (Cajaleo) mine in Riverside County, the Hogan-Mallery (Mecke-Hogan) mine in Kern County, and the Evening Star (Bernice, Rex) mine in San Bernardino County.

*Temescal Mine.* The Temescal (Cajaleo) mine and several neighboring properties which together comprise the Temescal tin district are confined to an area of approximately 15 square miles about 5 miles southeast of Corona and 11 miles southwest of Riverside. Here a mass of quartz monzonite, which has been mapped as a phase of the Woodson Mountain granodiorite, (Larsen, 1948, pp. 132-133, map) contains a group of tourmaline-quartz veins in only a few of which recoverable amounts of cassiterite have been found. Probably several hundred veins have been seriously explored in the Temescal district and numerous smaller stringers and tourmalinized zones also exist.

According to Page and Thayer (1945, p. 8) the average width of the veins, including spotted tourmaline rock and silicified rock, probably is 1 to 2 feet, although some of the veins are 6 feet wide, and in places a few are 15 to 20 feet wide. Most of the veins are less than 1,000 feet long and are discontinuous, although one vein system is about 4,800 feet long. The downward extent of the veins is not known but the Cajaleo vein was followed to a depth of 690 feet and was not bottomed. Most of the veins, including the Cajaleo vein, are in coarse-grained quartz monzonite, strike from about N. 20° E. to N. 50° E., and dip from 50° to 85° NW.

The Cajaleo vein is exposed on the surface discontinuously over a length of 550 feet and has been explored continuously over a length of 1,000 feet. It strikes about N. 55° E. and dips from 55° to 80° NW. On the surface, the vein is as much as 5 feet thick and, as exposed in the mine workings, ranges from 1 inch to 5 feet 10 inches. Maps of the mine indicate that two ore shoots were developed. One was about 70 feet and the other 160 feet in strike length, and the larger one had a dip length of about 240 feet (Page and Thayer, 1945, pp. 15-16, figs. 8, 11). The stopes, by means of which these shoots were mined, are now inaccessible.

The veins in the Black Rocks area, which is about 3 miles southeast of the Temescal mine, generally strike parallel to the Cajaleo system, but they dip southeastward. Southwest of the Temescal mine veins in dacite porphyry show wider divergence in attitude. Most of them strike nearly north and dip 50° to 70° W., but some of the larger ones strike N. 35° to 40° E., and dip 65° to 75° NW. In the areas between Cajaleo Hill and Lake Mathews, 1½ miles to the east, 10 additional major veins or vein systems have been recognized and extensively explored.

The veins are commonly zoned or banded, but most of the veins that are a foot or less in width consist entirely of mottled tourmaline rock or silicified rock. In the wider parts of the veins, where mineralization was more intense, their centers are occupied by a layer of fine-grained tourmaline a few inches wide. The veins

apparently replaced the quartz monzonite along fissures soon after it solidified. Assays indicate that almost all of the veins contain 0.03 to 0.1 percent tin, but samples assaying more than 0.1 percent have been collected in very few places. The Cajaleo vein averages about 0.15 percent of tin. The cassiterite occurs as disseminations and as bunches and stringers in the tourmaline-quartz rocks. The entire production apparently came from two connected cassiterite-bearing ore shoots in the Cajaleo vein. The ore that was milled is reported to have averaged in the range of 2 to 5 percent SnO<sub>2</sub> (Page and Thayer, 1945, 24 pp.).

The principal workings are at the Temescal mine and consist of an adit, a vertical shaft (the Robinson) now caved, an inclined shaft (the Williams or No. 1) that extends to a vertical depth of 540 feet, a raise to the surface from stope No. 1, and more than 5,800 feet of drifts and crosscuts on seven levels (Page and Thayer, 1945, p. 15). Other veins in the area have been explored by numerous shafts and adits with drifts and crosscuts. Considerable stripping and trenching also have been done on the veins.

*Hogan-Mallery Mine.* The Hogan-Mallery (Mecke-Hogan) mine and several neighboring tin-bearing properties are in the Gorman district of southern Kern County. These deposits are in small tactite bodies which have replaced limestone near the intrusive contact of a body of granitic rock. The cassiterite occurs as scattered grains within the tactite which is composed principally of limonite, magnetite, and various contact-metamorphic minerals.

The largest deposit, the Hogan-Mallery, is composed of two bodies of tin-bearing limonite gossan. The West gossan is about 200 feet in length and has a maximum exposed width of 40 feet, and lenses out at either end. The East gossan is 100 feet long and as much as 30 feet wide. The maximum thickness of the gossan is probably only about 25 feet beneath the surface.

According to Wiese and Page (1946, p. 37) the Hogan-Mallery mine was explored in 1942-43 by bulldozing and by sinking nine pits, each 10 feet deep, and two inclined shafts, each about 50 feet deep and joined to level workings that total about 150 feet in length. In addition, the property was core drilled and sampled partly by the U. S. Bureau of Mines in cooperation with the U. S. Geological Survey. Most of the high-grade ore was obtained from residual boulders exposed at the surface. Some was mined, by means of shallow pits, from pockets in limestone. The average grade of these small shipments was about 40 percent Sn. However, exploratory work indicated that reserves of ore in place carried only from 0.1 to 2.0 percent tin (Wiese, 1950, p. 46).

*Evening Star Mine.* The Evening Star (Bernice, Rex) mine and other nearby tin-bearing properties are about 8 miles north of Cima in northeastern San Bernardino County. The mine has explored a hematite pipe formed in limestone at the intersection of two fractures. Cassiterite is disseminated in the pipe, which is also reported to contain scheelite (Bedford and Johnson, 1946, p. 10; Tucker and Sampson, 1943, pp. 498-499; Wright et al., 1953, pp. 147-148; Hewett, 1956, p. 157, map).



*Other Properties.* Properties other than those in the districts mentioned above, and at which tin has been noted in quantities greater than one pound per ton of rock sample, include the following: The Lucky Three, Jeanette Grant, Black Jack, Rocky Point, and Big Blue properties in the Isabella district, Kern County; the Greenback Copper and Iron Mountain properties in the Woody district, Kern County; the American Flag and Monareh mines in the Elsinore district, Riverside County; and the Atolia tungsten mines, San Bernardino County (Bedford and Johnson, 1946, pp. 3-11).

#### HISTORY OF PRODUCTION

Tin was discovered in the Temescal district, Riverside County, prior to the Civil War, probably in 1853. A vertical shaft had been sunk 95 feet when the outbreak of the Civil War stopped the work. Exploration was resumed in 1868, and in 1869 a 15.34 ton shipment of ore to San Francisco was said to have yielded 6,895 pounds of tin (Page and Thayer, 1945, p. 1). However, the first production of record was in 1891. Ore was mined during 1891 and 1892 and later in 1928-29. In 1942 a modern 100-ton mill was erected and 1,400 tons of surface vein material was put through with a recovery of less than a pound of tin oxide per ton (Tucker and Sampson, 1945, p. 154). According to Segerstrom (1941, p. 543) approximately 113 long tons of tin were produced from the district. Page and Thayer (1945, p. 2) arrive at a figure of approximately 130.5 long tons, using data from Rolker (1895, p. 537) and Segerstrom (op. cit.).

In 1916, a property in Trabuco Canyon, Orange County, was partly explored in search of commercial quantities of tin, and a mill was erected, but no production was recorded (Segerstrom, 1941, p. 534). Tin was discovered in the Gorman district, Kern County, in 1940 and during the period 1943-45 the Hogan-Mallery (Meeke-Hogan) mine yielded 6.70 short tons of ore equivalent to 2.64 tons of tin. This was shipped to Metals Reserve Company (Wiese and Page, 1946, p. 33; Wiese, 1950, p. 46). Small shipments of ore and concentrates also have been made from the Evening Star mine of the Cima district, San Bernardino County (Tucker and Sampson, 1943, p. 498). The total California tin production that has been reasonably well documented is equivalent to about 117 long tons of tin metal, calculated on the basis of 100 percent recovery from concentrates. Even the maximum estimates indicate that the total output of tin from California has been less than 150 tons. In spite of numerous attempts during the last 50 years to develop tin mines in California, less than 4 percent of the tin produced in California was obtained in that period (Bedford and Johnson, 1946, p. 1). No tin production has been reported in California since 1945.

#### UTILIZATION AND MARKETS

The usefulness of tin is based upon its easy fusibility, malleability, resistance to corrosion, readiness to alloy with other metals, and its attractive silver color. Because of these properties, and the simplicity with which it can be recovered by smelting, it was one of the first metals to be used by man, particularly as a constituent of bronze. Today most of the tin consumed in the United States is used in plating material, solder, bronze, bearing metal, and foil. Smaller amounts are used in type

metal, pipe and tubing, chemicals, and for miscellaneous purposes (Vogelsang, 1949, pp. 81-83). During 1956, world mine output was 173,000 long tons of tin, while world consumption was 156,000 long tons. The United States consumption was 60,300 long tons (O'Connell, 1957, p. 94).

The price of tin has fluctuated over a wide range in the last 58 years. The average annual price has ranged from 13.67 cents per pound in 1897 to 127.07 cents in 1951. During 1956, the average price of "Straits" tin, New York, was 104.82 cents in January and 104.1 cents a pound in December, the annual average being 101.26 cents. The highest recorded price that has been paid for Straits tin on the New York market, 184.00 cents per pound, was reached on January 25, 1951. The rapid decline in the price of Straits tin in 1953 generated a strong movement among producers for an attempt to stabilize the price by international agreement which would ensure long-term equilibrium between supply and demand and thus provide stable marketing conditions for tin. The United Nations Conference on Tin, held in Geneva in December 1953, drafted the International Tin Agreement which provides for a buffer stock of 10,000 to 25,000 long tons and a tentative price range of \$0.80 to \$1.10 per pound, the buffer stock to be sold at \$1.00 or more and bought at \$0.90 or less. However, the United States had already indicated it would not necessarily adhere to the agreement (Harris and Trought, 1954) but they would also not oppose the agreement. This agreement was put into operation on July 1, 1956 (Renick and Umhan, 1956).

The nearest market for tin concentrates produced in California has been provided by the Government-owned Longhorn smelter at Texas City, Texas. If shipped from Los Angeles, which is 1,781 miles by rail from Texas City, the total rate in 1955 would have been \$14.06 to \$21.08 per ton in earload lots, depending on whether the material qualifies as crude or ground ore and is shipped in open or closed cars. The Longhorn smelter has been operated by the Tin Processing Corporation as an independent contractor under an operating agreement with the Reconstruction Finance Corporation. Under this arrangement the RFC purchased all concentrates, paid all operating costs, and sold the resulting tin. The Texas City tin smelter is not equipped to concentrate tin-bearing ores nor to treat concentrates containing less than 18 percent insoluble tin. In order to encourage domestic production of tin concentrates, lots as small as 650 pounds have been purchased. Congress authorized the Texas City smelter to continue in operation until January 31, 1957 (Public Law 608, June 22, 1956). Previously Congress had requested the President to conduct a study during 1955-56 of ways of maintaining a permanent domestic tin smelting industry, including continued Government operation of the facility or possible sale or lease to private industry (Senate Concurrent Resolution 26). In September 1955, the Office of Defense Mobilization authorized the Federal Facilities Corporation to negotiate the disposal of the smelter. Public Law 608 authorized the disposal of the plant by either sale or lease to private industry (American Mining Congress, 1956). Effective July 1, 1954, the operation of the smelter was transferred from the RFC to the Federal Facilities Corporation, a new agency established



in the Treasury Department. All purchases of tin concentrates by this corporation were made under formal contracts executed by both seller and buyer prior to shipment. The Office of Tin, Federal Facilities Corporation, Washington 25, D. C. made purchase arrangements. The Federal Facilities Corporation announced on January 3, 1957, that the Texas City tin smelter and other assets of the Government Tin Program had been sold to Wah Chang Corporation of New York. Wah Chang announced its intention to produce tin metal, tin alloys, and tungsten following extensive modification of the smelter whose operation was discontinued on January 31, 1957, pending completion of the modifications (American Mining Congress, 1957). A combined total of approximately 2.7 tons of tin contained in concentrates produced in California during the years 1943 and 1944 was purchased through depots operated by the RFC during those years. No program for Government purchase and stockpiling of tin ore is now (1956), in operation. However, pig tin meeting certain specifications has been purchased for the national stockpile. According to the Office of Defense Mobilization (1954, p. 14) the minimum objective for the national strategic stockpile for tin has been met.

#### EXPLORATION ASSISTANCE PROGRAM

Tin projects are eligible for assistance by the Defense Minerals Exploration Administration. The revised regulations as of March 23, 1954, list tin as eligible for the Government participation program with a Government contribution of 75 percent of the cost of an approved exploration program. By April 7, 1954, two applications for assistance under the DMEA program started in January 1951, had been received for tin projects in California. No tin contracts for California projects had been executed through April 1954.

#### MINING AND TREATMENT

Tin ore is mined by conventional methods used in placer and lode production of other metals. Most of the tin from the Far East and Africa is mined by dredges from alluvial or placer deposits. It is recovered as a high-grade concentrate of cassiterite which averages about 70 percent tin and is relatively free from impurities. The Bolivian tin-bearing veins require underground mining methods. The tin minerals in the lode deposits are more intimately associated with other minerals and more difficult to separate into a clean concentrate than in the placer deposits. Moreover, a large part of the tin in the original ore is lost during concentration. The ores as mined contain only a few percent of tin, so they must be milled to separate the gangue minerals and produce a concentrate containing 30 to 40 percent tin before they are shipped to the smelter. The losses of tin that occur during milling vary from 18 to 65 percent. The average recovery of tin from Bolivian ores is probably 50 to 60 percent (St. Clair, et al., 1954, p. 1).

Reduction of the oxide, cassiterite, is accomplished by a smelting process in which carbon is the reducing agent. Sulfide ores with a high sulfur content are roasted prior to smelting. The crude metal recovered by smelting is refined by electrolysis or by heat treatment. The world smelting centers are in British Malaya, United

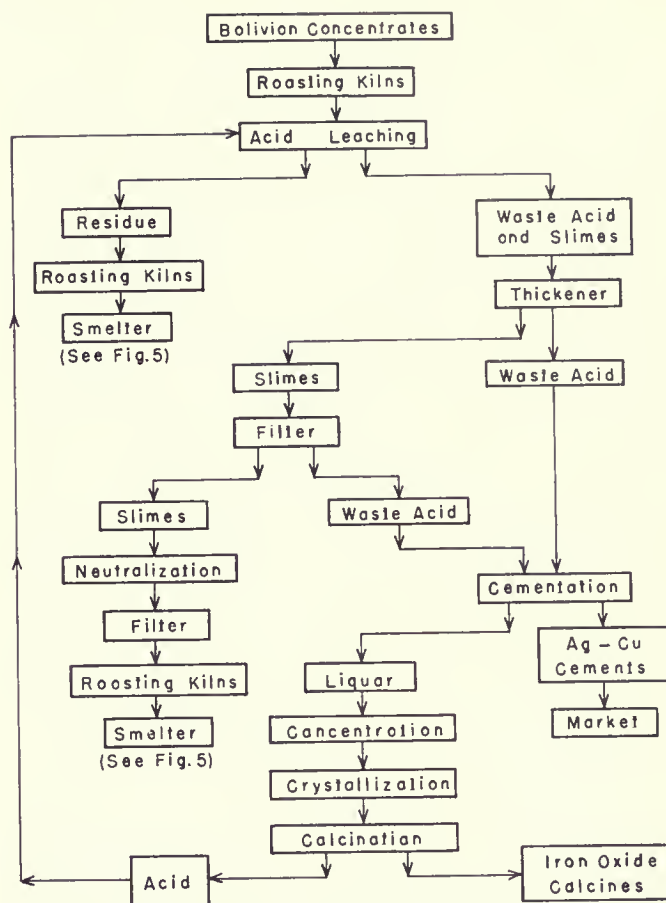


FIGURE 4. Flowsheet for Bolivian tin concentrates pre-smelting treatment, Longhorn tin smelter, Texas City, Texas. Adapted from Ridge et al., 1953, chapt. 7, sec. 4, p. 16-a.

Kingdom, Netherlands, Netherlands East Indies, and China. During World War II, all of the major tin smelters, with the exception of those in the United Kingdom, were subjected to occupation control by either the Germans or Japanese. This forced the allies to construct new facilities for the production of tin. The Longhorn smelter at Texas City, Texas, in the United States, was the most important new plant built and was placed in operation in April 1942. Impure concentrates, chiefly from Bolivia and lesser amounts from Indonesia, Thailand, Belgian Congo and miscellaneous sources are roasted and leached prior to smelting. Leaching plant products and pure alluvial ores are smelted in reverberatory furnaces. The rated annual output capacity is 45,000 tons. During 1956, the Texas City smelter produced 17,631 long tons of tin.

#### GOVERNMENT REGULATIONS

During World War II the Office of Production Management took control of all United States supplies of tin (Tin Conservation Order M-43, December 17, 1941). Subsequently many additional orders were issued to cover various phases of tin usage. Tin controls expired on December 1, 1949, with the exception of monthly tin reports which were required until June 30, 1950.

With the outbreak of the Korean conflict in 1950, concern again developed over the sufficiency of the



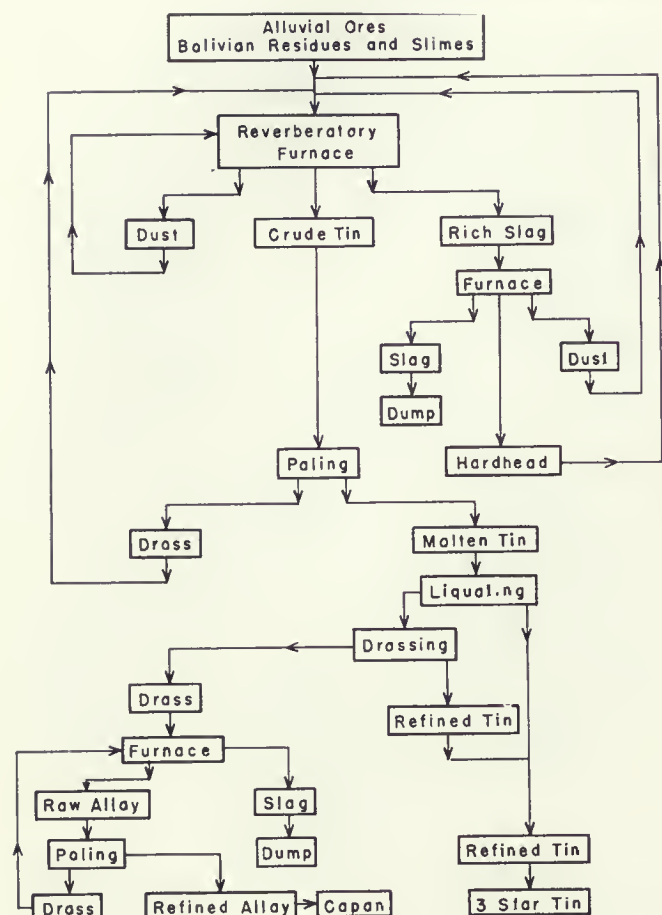


FIGURE 5. Flowsheet for alluvial tin ores and treated Bolivian tin concentrates, Longhorn tin smelter, Texas City, Texas. Adapted from Ridge et al., 1953, chapt. 7, sec. 4, p. 16-b.

United States' tin supply, and the National Production Authority issued order M-8 on November 13, 1950, to control the use of tin. The restrictions imposed were similar to those of World War II, but contained a few changes in methods of control. Allocation controls over pig tin were removed effective January 1, 1953. However, consumption continued to be restricted and limited by tin control order M-8 until February 6, 1953. On that date all controls over uses and inventories of tin were removed by the revocation of Orders M-8, M-24, M-25, M-26, M-27, and amendment of Regulation 1, inventory provisions. The decontrol of tin was made complete on February 13, 1953, when the Office of Price Stabilization removed the ceiling price on tin.

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# TITANIUM

BY PHILIP A. LYDON

Development of the titanium-metal industry has progressed rapidly in the last few years. Titanium dioxide has long been used in the pigment and ceramic industries, but only recently has relatively extensive use of the metal, especially in airplane manufacture, been possible. Although large, low-grade deposits of titaniferous magnetite in Los Angeles County are potential ore reserves, the total production of titanium ore in California has been quite small.

**Mineralogy.** Ilmenite ( $\text{FeTiO}_3$ ) and rutile ( $\text{TiO}_2$ ) are the principal ore minerals of titanium. Other titanium minerals include sphene ( $\text{CaTiSiO}_5$ ), perovskite ( $\text{CaTiO}_3$ ), benitoite ( $\text{BaTiSi}_3\text{O}_{10}$ ), arizonite ( $\text{Fe}_2\text{O}_3 \cdot 3\text{TiO}_2$ ), anatase or octahedrite ( $\text{TiO}_2$ ), brookite ( $\text{TiO}_2$ ), pseudobrookite ( $\text{Fe}_2\text{TiO}_5$ ), and leucoxene, a titanium-rich alteration product of the foregoing minerals. Commercial "ilmenite" commonly includes the minerals arizonite and leucoxene, and commercial "rutile" may include octahedrite, brookite, and pseudobrookite. Benitoite is a valuable gem mineral but is not an ore mineral of titanium.

Ilmenite is a black mineral with a metallic luster and black streak. It has a conchoidal to sub-conchoidal fracture, a hardness of 5 to 6, and a specific gravity of about 4.7. Ilmenite occurs in compact massive bodies, in veins, disseminated as single tabular crystals or small groups of crystals, and as loose grains in sand. Rutile is a black, red, brown, or yellowish mineral with a pale brown to yellowish streak, adamantine luster, and prismatic habit. It has a hardness of 6 to 6.5 and a specific gravity that ranges from 4.2 to 5.6. Rutile is a common minor constituent of schists, gneisses, and granitic rocks, and locally is a major constituent of beach and river sand.

The term "titanomagnetite" commonly is applied to an intergrowth composed of fine ilmenite lamellae in a matrix of magnetite ( $\text{FeO} \cdot \text{Fe}_2\text{O}_3$ ). The more general term "titaniferous magnetite" includes titanomagnetite as well as magnetite in which a small amount of titanium is carried in solid solution. Concentrations of titanomagnetite and/or ilmenite invariably contain minor amounts of chromium, vanadium, and phosphorus which affect the properties of iron, steel, and pigments produced from this material (Barksdale, 1949, p. 298).

**Geologic Occurrence.** All of the world's large ilmenite deposits are associated with basic-rock complexes composed of anorthosite, gabbro, and pyroxenite, and are related to them in origin. Anorthosite is an uncommon rock, generally light-colored and coarse-grained, that consists of plagioclase feldspar and less than 10 percent of dark pyroxene minerals, chief among which are augite and hypersthene. As the pyroxene content increases, anorthosite grades into gabbro or norite, which are darker, plagioclase-bearing rocks in which the principal pyroxene is augite or hypersthene, respectively. Gabbro and norite in turn grade into pyroxenite, a rock composed almost entirely of pyroxene minerals.

Iron-titanium mineralization is thought by many geologists to be of late-magmatic or hydrothermal origin (Hammond, 1952, Gillson, 1949, and Oakeshott, 1948). However, a comparison of chemical analyses of titanif-

erous ores with those of rocks typical of a normal sequence of crystallization suggests that at least some titanomagnetite is formed prior to the late-magmatic stage of crystallization. (See Wager and Mitchell, 1951, especially fig. 6 and tables 12 and F.)

Rutile deposits are associated with alkaline plutonic rocks such as nepheline syenite, aegerine phonolite, and jacupirangite, and with pegmatites and quartz veins. Sedimentary and metamorphic rocks derived from titanium-bearing igneous rocks may also contain concentrations of titaniferous minerals. Ilmenite, rutile, and titanomagnetite are heavy, resistant minerals and commonly are concentrated in beach sands and river placer deposits that also contain other heavy minerals, including zircon, monazite, magnetite, garnet, and staurolite.

The titanium ores that were mined in North America during 1954 were obtained principally from igneous-rock deposits at Sanford Hill in the Adirondack Mountains of New York, from Allard Lake in eastern Quebec, Piney River in Virginia, and Oaxaca, Mexico. Titanium-bearing beach sands near the east coast of Florida and river placer deposits in Idaho also were worked. Formerly, titanium ore had been produced commercially from Magnet Cove in Arkansas, Richland Cove in North Carolina, and from Roseland, Virginia. Nonproductive reserves of titaniferous minerals occur in Wyoming, Montana, Colorado, and New Mexico, as well as in California. Large deposits of rutile occur in Australia, Norway, Madagascar, and Brazil, and extensive reserves of ilmenite occur in Japan, Norway, Russia, and Ceylon. The titanium utilized by United States industry is obtained



FIGURE 1. Map showing location of San Fernando and Tujunga quadrangles (stippled). Part of this area is covered by geologic map of western San Gabriel Mountains in figure 2.









FIGURE 3. Titanium sponge and ingot produced by the U.S. Bureau of Mines at Boulder City, Nevada, using the Kroll process. Photo by Mary Hill.

chiefly from ilmenite mined at Sanford Hill and Allard Lake, and from rutile recovered from the beach sands of eastern Australia and eastern Florida.

At Sanford Hill, near the headwaters of the Hudson River, steeply dipping, tabular masses of almost pure ore consist of ilmenite, titanomagnetite, and minor amounts of rutile. The largest ore body is 1800 feet long and 900 feet wide. The ore at this mine averages 20 to 21 percent  $\text{TiO}_2$ , and 34 percent Fe. Estimates of reserves range up to 100 million tons of ore (Lawthers, 1955). The ore at Sanford Hill is mined by open-pit methods, and is trucked to a nearby concentrating plant capable of handling 5,000 tons of ore daily. Concentrates from this property are sent to National Lead Company's titanium pigment plants located in Sayreville, New Jersey.

At Allard Lake, Quebec, ilmenite-hematite deposits lie in an oval-shaped mass of anorthosite, 90 miles long and 20 to 30 miles wide. The Main orebody measures 3600 by 3400 feet at the surface and contains more than 100 million tons of proven ore averaging 32 percent  $\text{TiO}_2$  and 36 percent Fe. The Cliff orebody contains 12 million tons of proven ore of similar grade (Knoerr, 1952). The ore is mined by open pit and is carried 27 miles by railroad to Harve St. Pierre, on the St. Lawrence River. From here it is shipped by boat 550 miles upstream to Sorel, where the ore is crushed and smelted to yield a 70-percent  $\text{TiO}_2$  slag and a refined pig iron. The slag is sent to the Gloucester City, N. J., pigment plant of New Jersey Zinc Company, and in 1957 will also be sent to the projected pigment plant of Canadian Titanium Pigments, Ltd., at Varrennes, Quebec (American Metal Market, April 21, 1956).

Beach sand deposits of heavy minerals on the east coast of Australia for many years have been the principal source of rutile consumed in the United States.

Most Australian rutile is mined from modern and buried beach sands that extend for 50 miles across the Queensland-New South Wales border. These deposits contain an estimated 700,000 tons of rutile in relatively high grade deposits, and a minimum of 1.5 million tons of rutile in low-grade deposits (American Metal Market, Sept. 9, 1955). Australian beach sands are mined and treated by methods similar to those used in Florida.

Rutile and ilmenite have been produced from beach deposits in Florida near Melbourne, Jacksonville, and Starke. Recovery operations near Starke are on an old sand-dune deposit that averages a mile in width and extends from southern Georgia to south of Avon Park, Florida. In some places the ore-bearing sand is more than 30 feet thick (Speneer, 1948). Commercial concentrations within the sand contain an average of 1.76 percent ilmenite and leucoxene, and 0.28 percent rutile. A floating suction-dredge near Starke mines the sand to a depth of 35 feet at the rate of 1100 tons per hour (Thompson, 1952), and pumps it to barges where it is classified and concentrated. The bulk concentrate is dried and then separated by high-intensity electrostatic and magnetic separators.

Republic Steel Corporation reported early in 1955 (Eng. and Min. Jour., Jan. 1955, p. 118) that 27.5 million short tons of ore containing about 4.4 million tons of rutile had been proven on its property in the state of Oaxaca, Mexico. This property consists of 38 mining claims covering an area 7 miles long and  $1\frac{1}{2}$  miles wide, located 120 miles south of Oaxaca City. The rutile ore is hard but brittle, and occurs in three bands which average 40 feet in thickness.

*Localities in California.* Most of the titanomagnetite mined in California has been obtained from Los Angeles County, although beach sands near Aptos in Santa Cruz County were mined unsuccessfully during 1927 and 1928. The Los Angeles County output, approximately 15,000 tons in all, was recovered from sands at Redondo and Hermosa Beaches, from river sands in Sand Canyon in the western San Gabriel Mountains, and from a massive titanomagnetic deposit 2.4 miles southeast of Lang.

The first recorded attempt to utilize titaniferous ore in California occurred in 1906 at Russ Siding in Soledad Canyon, Los Angeles County, and ended in failure because of the refractory nature of the contained titanium. Activity in the area was confined to intermittent prospecting and exploration until 1927 and 1928, when the Lang locality yielded 10,013 tons of titanomagnetite. This ore was shipped to El Segundo for the manufacture of pigment, but was not competitive with less expensive foreign material. From 1927 to 1938, E. I. du Pont de Nemours and Company, Inc., conducted an extensive, systematic titanium-prospecting program in the San Gabriel Mountains. However, no ore was produced and the company's interests in this area eventually were abandoned. Since 1944, ilmenite produced in the San Gabriel Mountains has come mainly from titanomagnetite sands on the Live Oak and Ferro-Titan properties in lower Sand Canyon. This material has been used in the manufacture of paint base, as roofing granules, and in heavy aggregate.

The principal titanium-bearing deposits in California are masses of titanomagnetite associated with a body of pre-Cambrian anorthosite in the western San Gabriel



Mountains of Los Angeles County (fig. 1). Anorthosite and related gabbro and norite are exposed as an elongate, west-trending belt approximately 19 miles long and 7 miles wide, which is flanked on the north by Tertiary and Quaternary volcanic and sedimentary rocks, and on the south and east by pre-Tertiary plutonic rocks (fig. 2).

The San Gabriel anorthosite is a massive, minutely fractured rock, composed mostly of andesine plagioclase, that intrudes and grades into gabbro and gneissic diorite. All of the titanomagnetite bodies occur in either anorthosite or gabbro-norite, and most are within 2,000 feet of the mutual contact of these rocks. Masses of titanomagnetite range in size from small veinlets to large, tabular lenses. They bear no persistent relation to the topography and generally are moderately to steeply dipping. Some of these deposits are very irregular in shape, although most are lenticular. The larger masses are elliptical in plan. The largest single body of titanomagnetite is 1000 feet long and 800 feet wide at the outcrop; it is estimated to contain 250,000 tons of rock averaging 11 to 25 percent  $\text{TiO}_2$  (Oakshott, 1948). In all, the San Gabriel Mountains probably contain several million tons of titaniferous rock with 5 to 20 percent  $\text{TiO}_2$ . This material, however, is scattered throughout scores of small bodies irregularly shaped or with gradational boundaries. Even in the areas of richest mineralization, many of the bodies are so scattered that they would be difficult to mine.

In thin section, the titanomagnetite is seen to be closely associated with the most thoroughly granulated or altered rock. It has replaced hornblende along cleavage planes, and similarly penetrates or embays biotite, epidote, clinozoisite, chlorite, actinolite, apatite, and feldspar. Grains of titanomagnetite average less than 1 mm. in diameter and consist of fine lamellae of ilmenite developed parallel to crystal directions in magnetite, although in intergrowths that are especially rich in ilmenite, it forms relatively large, irregular patches. Ilmenite and magnetite in the intergrowth occur in proportions ranging from 1:5 to 3:4 (Oakshott, 1949). Because of the very fine size of the ilmenite lamellae, a satisfactory ilmenite-magnetite separation has not been achieved by mechanical means.

At the Live Oak mine in Sand Canyon, a modest though consistent producer, titanomagnetite is recovered from naturally concentrated heavy sands which extend along the creek bed for more than 2500 feet. This sand averages 7.5 percent  $\text{TiO}_2$ . The Paeoima Creek placer deposit contains notable amounts of black sand for 4000 feet along the length of the creek. Pits indicate that alluvium in which the heavy sand occurs commonly is more than 40 feet deep. Analyses show that the grade of most of this material lies within the range of 2.4 to 30.8 percent  $\text{TiO}_2$ . The full extent of reserves in these placers is not known because they have not been systematically explored and sampled, but they appear to contain several million tons of workable titaniferous sand.

A small deposit of rutile has been reported west of Barstow in San Bernardino County (Wright, et al., 1953, and Youngman, 1930, p. 5). Small crystals of rutile, locally concentrated and banded, are disseminated along 200 feet of an irregular, lenticular body of quartz in schist. The quartz itself is 1500 feet long and has a maximum width of 75 feet.

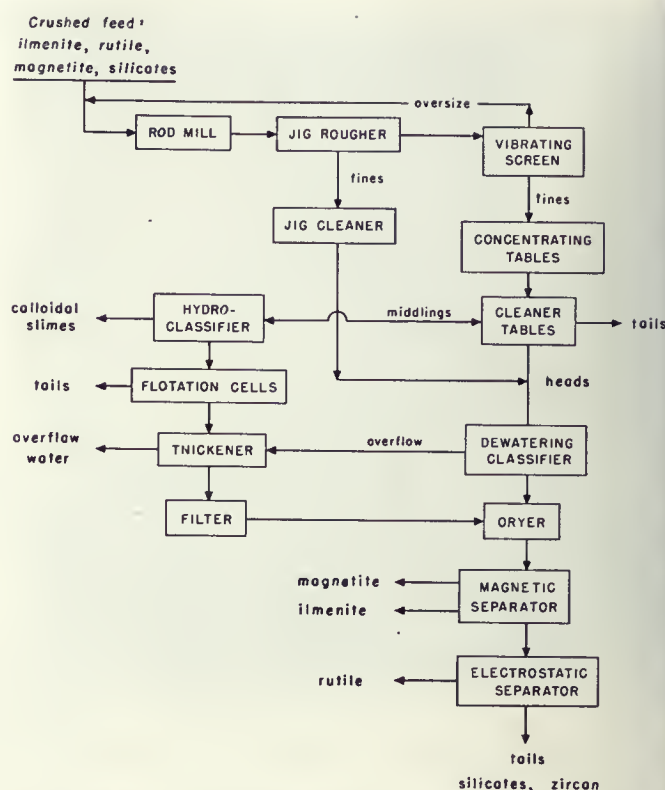


FIGURE 4. Generalized flow sheet for milling titaniferous ore rock. Adapted from figure on page 17, *Deco Trefoil*, courtesy of Denver Equipment Co., Sept.-Oct. 1955.

Beach-sand deposits that have been worked for their titanium content occur between Redondo Beach and Palos Verdes Point in Los Angeles County (Tueker, 1927), and along  $1\frac{3}{4}$  miles of beach southeast of Aptos in Santa Cruz County. The deposits in Los Angeles County are distributed along about  $2\frac{1}{2}$  miles of beach. Near Clifton, these sands average 7 percent ilmenite for a distance of 3000 feet (Baughman, 1927, p. 310). Some concentrations of almost pure ilmenite and magnetite contain these minerals in a 3:2 ratio. Titanium minerals at this beach occur in lenticular bodies of heavy sand that are about 5 feet thick, 100 feet wide, and 150 feet long. The sand near Clifton was worked in 1927, and was reported to contain 20 percent "titaniferous iron" and magnetite, and a residue of silica, olivine, epidote, garnet, and zircon (Tueker, 1927).

The deposits near Aptos in Santa Cruz County are in strata that range from a few inches to several feet thick, and occur on both the present beach and older marine terraces away from the shore line (Hubbard, 1943). The sand contains magnetite, chromite, ilmenite, garnet, zircon, quartz, and a small amount of gold. Irregular crescents of black sand, 100 or 200 feet long and up to 50 feet wide, occur along the foot of detrital bluffs and are said to be mostly magnetite, with some martite (isometric  $\text{Fe}_2\text{O}_3$ ), and 16 percent  $\text{TiO}_2$  as ilmenite (Youngman, 1930, p. 4).

*Treatment.* Beneficiation processes that separate titanium-bearing minerals from other heavy minerals and gangue generally are simple and are based principally



on differences in specific gravity and magnetic and electrostatic susceptibility (fig. 4).

All of the titanium metal produced commercially in the United States during 1955 was obtained by methods based on the Kroll process, which involves the reaction of liquid titanium tetrachloride with molten magnesium in an inert atmosphere to form a spongy mass of metallic titanium resembling coke. Crude titanium tetrachloride is made by reacting a mixture of titanium minerals and carbon with chlorine gas at high temperature. Any iron present in the feed will be converted to ferric chloride, thereby increasing the non-recoverable consumption of chlorine and the difficulty of producing a pure titanium tetrachloride. At the Titanium Metals Corp. of America plant in Henderson, Nevada, magnesium chloride, a by-product of this reaction is recovered and treated electrolytically to yield magnesium metal and chlorine. After separation of the magnesium chloride, the sponge is purified by double-melting to ingot form in vacuum furnaces.

Because of the necessity of controlling contamination in all stages of titanium metal manufacture, rutile is the preferred feed for production of the metal. Although rutile concentrates are the most expensive available raw feed for this use, its cost per pound of contained titanium is competitive with that of other feeds (table 2), and is superior when decreased costs of treatment are considered. Titanomagnetite, which has a low titanium content, is unsuitable for the manufacture of either titanium metal or pigment base because of the increased cost caused by production of excessive ferric chloride or sulfate.

Titanium dioxide of pigment grade can be produced from titanium concentrates by many methods. Of these, the sulfate and chloride processes, in which ilmenite or titanium-rich slag is dissolved in sulfuric or hydrochloric acid, are most commonly used. The resulting solution contains a large proportion of iron compounds and other impurities, but hydrous titanium oxide of high purity is precipitated by thermal hydrolysis. In the chloride process, iron compounds usually are removed before hydrolysis. Ilmenite and Sorel slag are used as feed in pigment manufacture because of their abundance and relatively low cost.

Titanium-rich slag and pig iron are produced at Sorel, Canada, by the Quebec Iron and Titanium Corporation which uses a low-flux, continuous-feed process. The raw material is ilmenite-hematite ore mined at Allard Lake. Each 1000 tons of ore is combined with approximately 143 tons of a coal flux and is expected to yield about 440 tons of 70-percent  $\text{TiO}_2$  slag and 320 tons of crude iron (Knoerr, 1952). Because no lime flux is used in the smelting process, sulfur and other impurities in the crude iron are removed in an electric-arc refining furnace.

During 1954, Foote Mineral Company produced a few hundred pounds of pure titanium metal on an experimental basis by thermal decomposition of titanium iodide gas, and Metal Hydrides, Inc., produced about a ton of titanium-metal and -hydride powder by reduction of titanium dioxide with calcium hydride (Tumin, 1955).

Pilot-plant production of titanium sponge in which sodium rather than magnesium is used in the reduction

process began in Great Britain in 1954. In 1956, a plant utilizing sodium was completed at Ashtabula, Ohio, by Electro Metallurgical Company. Experimentation with other methods of titanium-metal production continued into 1956, and included vapor deposition, alkali-amalgam reduction of the tetrachloride, and reduction of the tetrachloride by hydrogen in a molten bath (Oldham, 1956). That same year, the U. S. Bureau of Mines announced the success of an experimental electrolytic process for recovering premium-grade titanium metal from scrap (Eng. and Min. Jour., Apr. 1956, p. 101). Electric smelting tests, conducted by the Bureau of Mines on placer ilmenite concentrates from Idaho, indicated that a high-titanium slag and a good grade of pig iron can be produced from such material (Banning, et al., 1955).

Titanium is a highly reactive metal which, when heated in the presence of oxygen, nitrogen, or hydrogen, absorbs these elements and, owing to contamination and embrittlement, undergoes a marked decrease in ductility. In order to avoid this, it is necessary to anneal titanium in a vacuum or in an inert atmosphere of argon or helium. It deteriorates at continued temperatures in the range 800° to 1,000° F., but this appears to be almost entirely a surface effect. Laboratory and field tests have shown that the usefulness of the metal can be increased in certain instances by coating its surface with non-absorptive elements such as chromium and molybdenum.

The properties of titanium metal are affected by its crystal structure, of which there are two types. Alpha titanium, the low-temperature form, is stable up to 1615° F. and has a hexagonal close-packed structure similar to that of magnesium. Beta titanium, the high-temperature form, is unstable below 1615° F. and has a body-centered cubic structure.

Alpha titanium is not as ductile as beta titanium. This is unfortunate because, if the low-temperature form were the more ductile of the two, the cold metal would be easier to work, and the reactive nature of the heated metal would be less bothersome. The more ductile beta phase, however, can be stabilized by adding small

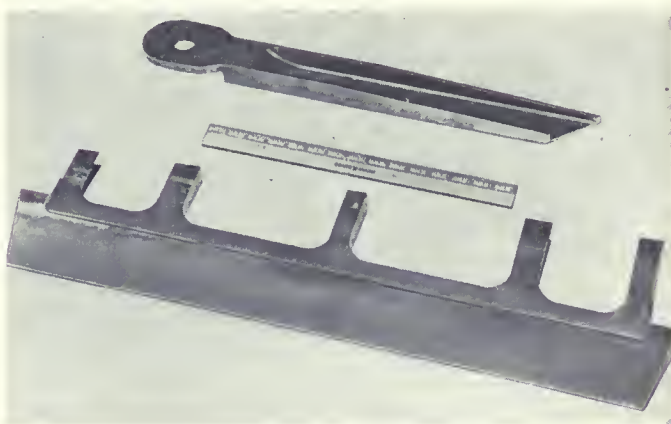


FIGURE 5. Titanium sections of the wing-support assembly of the Convair F-102 are made from alloyed titanium forgings. The alloy (Rem-Cru C-130AM) contains 4 percent each of aluminum and manganese, has a combined alpha-beta structure, and has a minimum yield strength of 130,000 pounds per square inch. Photo courtesy Rem-Cru Titanium, Inc., from *Rem-Cru Titanium Review*, Jan. 1955.



amounts of iron, chromium, or manganese, thereby preventing a complete beta-to-alpha inversion upon cooling below 1615° F. Beta-stabilizing elements substitute for titanium atoms only in the beta phase, and so have no effect on the alpha phase. High-strength, titanium-base alloys currently on the market contain 2 to 8 percent of these or similarly acting elements.

Alpha titanium is weaker than beta at 700° F., the operational temperature best suited to the metal. Here, the alpha phase can be strengthened by adding very small amounts of oxygen, nitrogen, or carbon, atoms of which concentrate in the alpha phase and occupy interstitial positions in the crystal lattice.

*Utilization.* Approximately 99 percent of the 780,097 short tons of ilmenite concentrates and titanium slag consumed in the United States during 1954 was used in the manufacture of high-opacity pigments for paints, enamels, and glazes (Tumin, 1955). Titanium-dioxide powder is an exceedingly opaque material that weathers and discolors less rapidly than other paint bases. Its whiteness, high refractive index, chemical stability, and relative cheapness also contribute to its usefulness as a pigment base. The characteristics of titanium-dioxide pigment can be modified by the addition of various combinations of extenders and additives.

In 1954, about 21 thousand tons of rutile were consumed in the United States, and were used chiefly for titanium metal, alloys, and carbide, and for welding-rod coatings. Smaller quantities were used in ceramics, chemicals, and fiberglass (Tumin, 1955). Titanium metal is useful because it is intermediate between aluminum and stainless steel in its density, modulus of elasticity, and elevated-temperature strength. In addition, it is a highly refractory material (melting begins at approximately 1,725° C.), is resistant to corrosion by sea water and many chemicals, and has a low rate of thermal conductivity and a low coefficient of expansion.

A small but important use of titanium is as a minor alloying constituent with other metals in iron. Titanium in high- and medium-carbon ferroalloys is used chiefly to deoxidize steel or to control its grain size. Low-carbon ferrotitanium alloys are used to stabilize carbon and nitrogen in various types of steels, whereas ferrosilicon-titanium alloys are added to iron to produce low-alloy, high-strength steels. Titanium is added to medium manganese steel, widely used for high-strength railroad castings, in order to refine the grain size and thus reduce air-hardening. The weldability, short-time creep strength, and stress-rupture ductility of chromium-molybdenum steels are improved by the addition of titanium.

The use of pure or alloyed titanium metal is increasing as extractive processes and metal-working techniques are improved. Because titanium metal functions well at moderately high temperatures, is lighter in weight than an equivalent volume of stainless steel, and has good wearing properties, it has been designed into commercial and military aircraft parts such as bulkheads, shroud assemblies, ammunition tracks, fasteners, and jet tailpipe aspirators.

Titanium and titanium alloys, however, are not only planned for aircraft still on the drawing boards, but are used in current operational models of certain military and civilian aircraft. The Douglas Aircraft DC-7, for

example, uses more than 350 pounds of titanium in the engine-nacelle skin and firewall webs, and the DC-7C uses more than 850 pounds of titanium in the airframe (American Metal Market, Feb. 2, 1956). Titanium alloys are used in the front compressor case and the intermediate case of the J-57 turbojet engine, and unalloyed titanium is used in the inlet case. This engine is used in such aircraft as the Boeing B-52 Strato Fortress, the North American F-100 Super Sabre, and the McDonnell F-101 Voodoo. The Convair F-102, also powered by a J-57 engine, uses 400 pounds of titanium and its alloys in ducts, leading-edge ribs of the wings, the fuselage frame, the engine area, and in wing-spar fittings (fig. 5).

Titanium dioxide finds a limited use in the manufacture of electrodes for electric-arc lamps. Small amounts of titanium alloys and compounds are used in electrodes and filaments of electron-discharge tubes, negative elements of thermocouples, and in the ignition electrodes of electrical-resistance heaters. Very finely ground rutile or sphene is used in extruded electric welding rods in order to stabilize the arc and reduce viscosity in the welding slag. Ground titanium dioxide is a major component of sintered ceramic- or organic-bonded electrical insulating materials.

Titanium tetrachloride is used in smokescreens and skywriting. However, because titanium-tetrachloride clouds dissipate more rapidly than those produced from white phosphorous or oleum, this material has had only limited military application. Small amounts of powdered titanium metal are used in pyrotechnics because of the brilliant white light produced by its combustion.

As a water-purifier coagulant, titanate sulfate is superior to aluminum and ferric sulfates in its ability to remove color and yield good flocs over a wide range of hydrogen-ion concentration. Titanium tetrachloride is used as a flocculating agent in sewage treatment, and titanium dioxide is used to remove fatty acids from laundry wastes.

Titanium dioxide (refractive index approximately 2.7), added in small amounts to paper, provides a high degree of opacity and a natural white tone in the finished product.

Non-reflective rayons are made by incorporating a chemically inert pigment such as titanium dioxide into the viscose solution from which the rayon fibers are spun. Reflection is kept to a minimum, as diameters of the titanium dioxide particles are less than the average wavelength of visible light. Such particles produce an interference effect in the incident light, part of which is then absorbed by the pigmented surface.

Various titanium compounds are used as mordants, or dye-fixing agents, in the textile industry. In addition, titanium tannate is used as a dye to produce shades of yellow on mercerized cotton, and trivalent salts of titanium are used to strip dyes from cotton, wool, and silk. Potassium-titanium oxalate is used as a mordant or to produce a stable, yellowish-brown color in leather goods.

A small proportion of relatively pure titanium dioxide is added to artificial teeth to provide a natural yellowish tint. Synthetic star sapphires and rubies are made by fusing powdered aluminum oxide containing minute quantities of purified titanium dioxide. As a minor constituent of various compositions of glass, titanium dioxide promotes acid resistance, retards devitrification, and







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# TUNGSTEN

By RICHARD M. STEWART

Commercial production of tungsten ore in California began in 1905. During the period 1905-54, deposits in the state yielded a total of about 54,000 tons of concentrates containing a minimum of 60 percent  $WO_3$ . This output represents slightly more than 30 percent of the nation's total production and had a total value of about \$98,000,000. In 1954, sources in California yielded 3,512 tons of concentrates, and California was second to Nevada as a domestic source of tungsten ore. Moreover, 1954 was the first year in which the value of the tungsten concentrates produced in California, \$13,209,371, exceeded the value of any other metal produced in the state during the same year.

**Mineralogy and Geologic Occurrence.** Tungsten does not occur free in nature and is a constituent of relatively few minerals. Of the 14 known tungsten-bearing minerals, the only ones of commercial importance are scheelite ( $CaWO_4$ ) and the three minerals in the isomorphous wolframite series—ferberite ( $FeWO_4$ ), wolframite ( $Fe,MnWO_4$ ), and huebnerite ( $MnWO_4$ ). Most of the world's tungsten output is obtained from scheelite and wolframite. Ferberite is the principal mineral in most productive tungsten deposits of Colorado; huebnerite seldom is found in commercial quantities.

Scheelite is a light-colored mineral, ranging from white to gray to light shades of yellow, green and reddish- or orange-brown. Its luster ranges from greasy to vitreous. It is heavy (specific gravity, 5.9 to 6.1), moderately hard (4.5 to 5), brittle, and breaks either with an uneven to sub-conchoidal fracture or along one distinct cleavage plane.

Scheelite contains 80.6 percent  $WO_3$  when pure, and is the principal tungsten mineral in California. It is most easily recognized by a bright bluish-white fluorescence under ultra-violet light. Molybdenum can substitute for part of the tungsten in the scheelite formula, and a partial isomorphous series extends toward powellite [ $Ca(Mo,W)O_4$ ] at least to a molybdenum-tungsten ratio of 1 to 1.38 (Palache, 1951, p. 1075). As the molybdenum content increases, the color of the fluorescence changes from blue-white to white to yellowish-white.

The presence of tungsten can be detected by boiling a powdered sample of a tungsten-bearing material in strong hydrochloric acid. If an appreciable amount of tungsten is present, a lemon-yellow residue of tungstic acid will form. This residue will dissolve if an excess of ammonia is added. Tin or zinc added to hydrochloric acid that contains dissolved tungsten will cause the solution to turn successively blue and brown.

Though tungsten deposits have formed under widely different conditions of temperature and pressure, they characteristically occur in or near bodies of acidic igneous rocks. Tungsten minerals commonly are scattered through igneous rocks, particularly pegmatite and aplite dikes, but few of these occurrences are of economic interest. Most commercially valuable concentrations of tungsten minerals have formed in veins and replacement or contact metamorphic bodies that are near igneous masses.



FIGURE 1. Chart showing amount of tungsten concentrates (60 percent  $WO_3$ ) produced in California and average price per unit, 1905-1955.

Most tungsten-bearing veins are rich in quartz and commonly contain both scheelite and wolframite. In many of the higher-temperature veins, the tungsten minerals are accompanied by cassiterite ( $SnO_2$ ); in many of the medium- and lower-temperature veins, such minerals as pyrite ( $FeS_2$ ), chalcopyrite ( $CuFeS_2$ ), sphalerite ( $ZnS$ ), and galena ( $PbS$ ) are present. The scheelite-rich quartz veins of the western United States, such as those at Atolia, California, contain no wolframite. The wolframite-quartz veins of Colorado (Hess and Schaller, 1914; Lovering, 1940) and South Dakota (Irving, et al., 1904, pp. 163-169) contain only minor proportions of scheelite.

Most of the tungsten mined in California in recent years has been obtained from contact-metamorphic deposits. Eighty-five percent of all of the known deposits are in tectite (Bateman and Irwin, 1954, p. 34) which is "a rock of more or less complex mineralogy formed by the contact metamorphism of limestone, dolomite or other soluble rocks into which foreign matter from the intruding magma has been introduced by hot solutions or gases" (Hess, 1918, p. 378). The most common minerals in tectite deposits are reddish-brown garnet of the grossularite-andradite series, epidote, green pyroxene (diopside-hedenbergite series), quartz, and calcite. Scheelite is by far the most abundant tungsten mineral in tectite bodies, but commonly shows an irregular distribution. In California many tungsten-bearing tectite bodies contain appreciable proportions of molybdenite and copper minerals. Tectite bodies characteristically are irregular in shape in contrast with the tabular, tungsten-bearing vein deposits.





FIGURE 2. Map of California showing distribution of tungsten deposits. Data from published and unpublished reports of California Division of Mines and unpublished reports of U. S. Geological Survey.



Because some tungsten minerals are resistant to weathering, they are readily concentrated in placer deposits. For many years the wolframite placers of China were the world's principal source of tungsten. As scheelite is brittle and easily reduced to slime, it ordinarily does not accumulate in placer deposits. Those that do exist are closely associated with their sources and consist of coarse-grained material. The scheelite placers in the Atolia district of California are among the few examples of this type.

**Localities in California.** California, with the possible exception of Nevada, contains more tungsten-bearing localities than any other state. Most of these are confined to the areas intruded by the Sierra Nevada batholith, of Mesozoic age, or satellite bodies related to it. Tungsten deposits are particularly abundant along the east and west borders of the batholith from Kern and San Bernardino Counties northward to Madera and Mono Counties. They are relatively sparse in the northern portion of the batholith area. Tungsten-bearing taconite deposits also are associated with isolated bodies of granitic rock that lie farther east (Bateman and Irwin, 1954, p. 34). Tungsten deposits of proved commercial value have not been discovered in the Coast Ranges or Klamath Mountains.

Throughout the tungsten-bearing belt, metamorphosed sedimentary rocks, older than the batholith, border the igneous bodies, or are completely surrounded by them. The vein deposits, such as those at Atolia, are distinctly later than the enclosing granitic rocks.

Most of the tungsten ore produced in California has been obtained from two areas, the Atolia district in San Bernardino County, and the Bishop district in Inyo County. The Atolia district was the principal source of tungsten ore annually in the state until 1938, when it was surpassed by the Bishop district.

The primary tungsten deposits in the Atolia district (Lemmon and Dorr, 1940, pp. 205-245) consist of a group of steeply dipping veins that contain scheelite in a quartz-carbonate gangue. They have formed along fractures in Mesozoic quartz monzonite. The known veins in the district are confined to an area that is about two miles long and 500 feet wide. The six most productive mines have exploited a total of 11 veins, but most of the tungsten ore was obtained from two of these—the North and South veins in the Union mine.

The veins of the Atolia district were deposited in open fissures, and the wall rocks show little alteration. The scheelite is confined largely to nearly vertical shoots, most of which are thickest near the surface and taper downward. The width of the ore bodies ranged from a few inches to 17 feet. The largest of the known ore shoots was encountered in the South vein in the Union mine; this had a maximum exposed horizontal length of 1,260 feet and a pitch length of 1,080 feet. The other ore shoots in the district have proved much smaller, and have averaged about 100 feet in length. The Union mine was productive to a depth of 1,021 feet but most of the veins in the district pinched out at depths of 170 feet to 260 feet.

Some large masses of nearly pure scheelite have been found, but from 1909-40 the average grade of the ore mined each year ranged from 1 to 15 percent  $WO_3$ , and the overall average grade has been 4.14 percent  $WO_3$ .

The Atolia veins are the source of the scheelite in the extensive placer deposits nearby. The placer area east of the vein deposits, which is known as the Spud Patch, has yielded most of the placer scheelite. Here most of the scheelite ranges from material the size of fine sand to fragments ("spuds") the size and shape of potatoes, but some of the fragments weighed several hundred pounds. The richest scheelite concentrations are in well-defined channels. These have been mined by underground methods, and in later years by stripping and large open

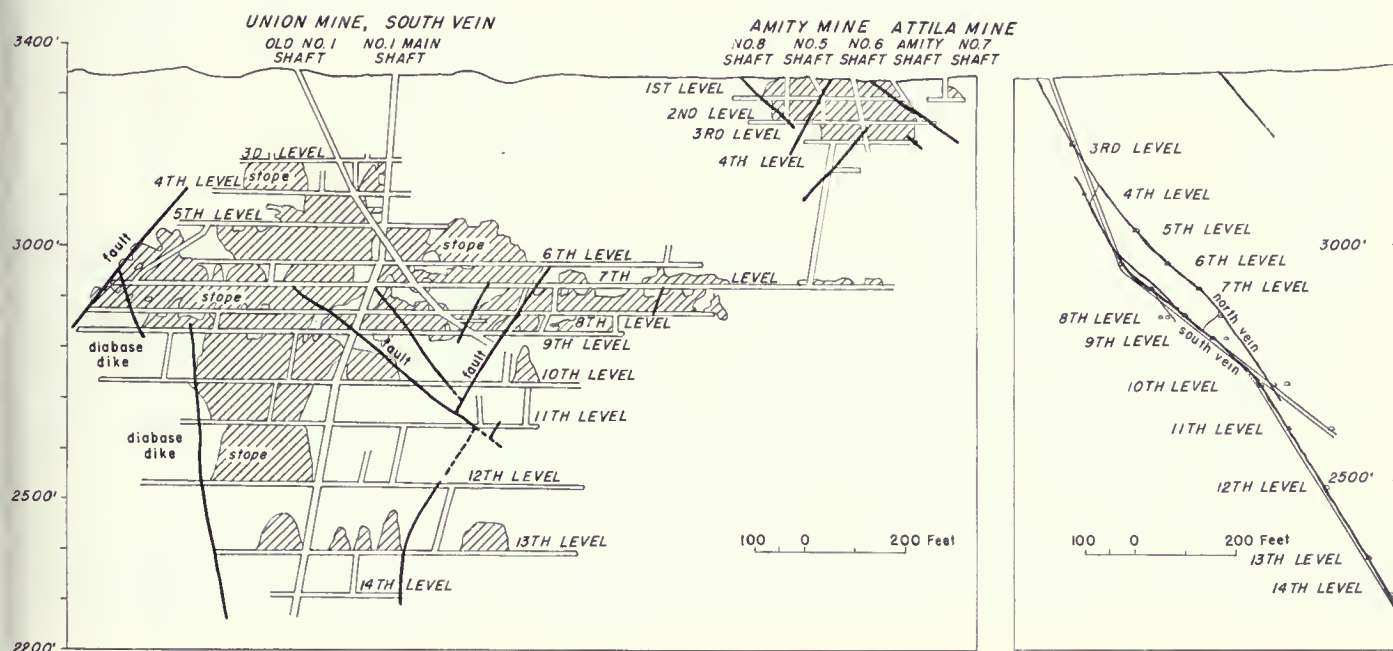


FIGURE 3. Sections through the Union and Amity mines, Atolia district. After D. M. Lemmon and J. V. N. Dorr, 2nd, 1940.



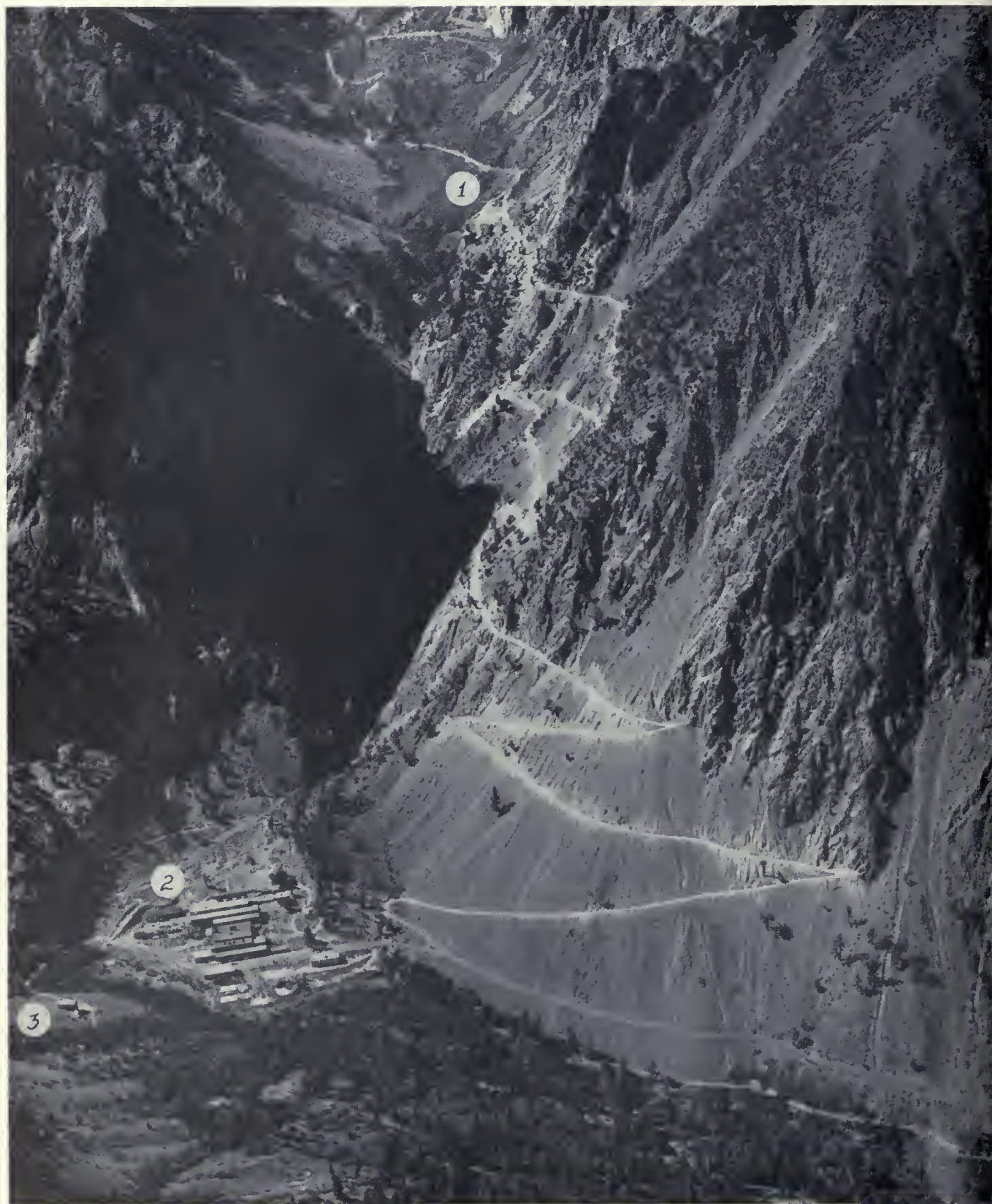


FIGURE 4. Pine Creek tungsten mine area, Inyo County, showing (1) portal of Zero (1500) level, (2) Pine Creek mill, and (3) terminal of aerial tram from Brownstone mine. *Photo courtesy Curtis Phillips, Bishop.*



pit operations. The channels have been worked laterally for distances of as much as 4,000 feet. A placer area to the west of the vein deposits has been worked primarily for gold, but scheelite has been obtained as a by-product.

The tungsten deposits in the Bishop district are distributed along the eastern slope of the Sierra Nevada and in the lower foothills called the Tungsten Hills. This district, which extends from Round Valley southward for about 20 miles and also includes the Pine Creek area to the west, has been a source of tungsten ore since 1916. To the end of 1953, the output from the district has totaled about 1,300,000 units of  $WO_3$ , most of which was obtained from the Pine Creek mine (Bateman, 1956) during the period 1942-53.

The Pine Creek mine, operated by the Union Carbide Nuclear Company (formerly the United States Vanadium Company), contains the largest known reserve of tungsten ore in the United States (Bateman, 1945, p. 233) and also is a source of molybdenum, copper, and gold. The ore bodies are near the north end and on the west side of the Pine Creek pendant, an elongate mass of metamorphic rocks which is surrounded by granite and quartz monzonite. The pendant, which is about  $5\frac{1}{2}$  miles long and 1 mile wide, is composed of hornfels, schist, quartzite, and marble. The marble occurs chiefly in a  $3\frac{1}{2}$  mile belt on the west side of the pendant.

Tungsten ore is confined to bodies of garnet-diopside tectite that occur in a north-trending contact zone between the granitic rock and marble. The contact zone also contains bodies of quartz and quartz-feldspar rock. Scheelite is the only primary tungsten material. Molybdenite ( $MoS_2$ ) is present in all the known ore bodies, and some ore, although scheelite-bearing, was mined primarily for its molybdenite content (see section on molybdenum in this bulletin). Powellite [ $Ca(Mo,W)O_4$ ] (an oxidation product of molybdenite), bornite ( $Cu_5FeS_4$ ), and chalcopyrite ( $CuFeS_2$ ) are present in minor proportions.

Bateman (1956), whose recent report is the source of most of the following description of the Pine Creek mine, defines an "ore body" here as a mass of tectite containing scheelite-bearing ore shoots. Five separate ore bodies lie along a 3,000-foot segment of the contact zone. The greatest horizontal separation between adjacent bodies is about 350 feet. They total about 1,000 feet in combined length. Listed from south to north, these are the South, Main (formerly North), Pinnacle, North (formerly Level E), and Loop ore bodies. The Pinnacle ore body is entirely enclosed in marble; the rest are along the contact between marble and the quartz monzonite.

The size and spatial relationships of the ore bodies are indicated by the nature of the mine workings. The main adits and their altitudes are:

Level C	11,215 feet
Level A	10,940 feet
Zero (1500) level	9,430 feet

Sub-levels have been driven between Levels A and C and the surface, and an internal shaft was sunk 250 feet from Level A. The mine can be considered in two parts. The "old mine" consists of all the workings, including surface cuts, about Level A. The second part, the source of all ore mined since 1951, consists of all workings between Level A and Zero level.

The South ore body was 300 feet by 150 feet in outcrop dimensions but was only 50 feet thick on Level A and 15 feet thick in a diamond drill hole 600 feet below Level A. It was not identified in the Zero level. The South ore body was occupied almost completely by a single ore shoot that had an average grade of 0.75 percent  $WO_3$ .

The Main ore body, about 300 feet northeast of the South ore body, had an outcrop plan 300 feet long with an average width of 50 feet. This body is remarkably persistent through a vertical distance of at least 2,170 feet. In horizontal sections, its length ranges from 350 to 600 feet and its width from 30 to 200 feet. Its maximum plan, just above Zero level, was 600 feet long and 200 feet wide near the center. The ore shoots are tabular, concordant with the ore body and have the greatest dimension vertically; some have been persistent through several hundred feet. Above Level A, the ore shoots comprised 40 percent of the tectite. Between Level A and Zero level they comprise 70 percent of the tectite.

The Pinnacle ore body extends from the Main body several hundred feet northward, but only a part of the outcrop, which is 160 feet long and 25 feet wide, contains minable amounts of tungsten. This deposit has not been mined.

The North ore body is actually a group of smaller bodies lying about 1,000 feet north of the Main body. It has been mined on the surface and underground but was a relatively small source of ore. The Loop ore body has been explored only by open cuts.

The configuration of the ore shoots is determined by assay; 0.40 percent  $WO_3$  and 0.40 percent  $MoS_2$  are the assumed cut-off grades. The shoots have fairly sharp boundaries and are not surrounded by large tonnages of marginal grade ore. During the period 1942-44, when the exploitation of the deposits above Level A was at the peak, mill heads averaged 0.45 percent  $WO_3$ , 0.20 percent  $MoS_2$  and 0.12 percent copper. During the period 1949-53, when all the ore was from the Main ore body above the Zero level, the mill heads averaged 0.52 percent  $WO_3$ . During a single year, 1952, ore from the Zero level workings averaged 0.52 percent  $WO_3$ , 0.12 percent  $MoS_2$  and 0.05 percent Cu (McKinley, H. L., 1953, personal communication).

The total production of the Pine Creek mine to the end of 1953 is 1,057,498 units of  $WO_3$ , 6,130,559 pounds of molybdenum, 1,967.97 tons of copper and 670 ounces of gold recovered from smelting. The total production from the Bishop district is on the order of 1,300,000 units of  $WO_3$ .

The Black Rock mine, south of Benton in Mono County, also is an important source of tungsten ore. The metamorphosed sediments in the mine area have been folded into a north-plunging, asymmetric anticline having a core of marble and tectite and limbs of overlying schist (Lemmon, 1941, p. 587). The east limb dips more steeply than the west limb. The latter has been intruded by a mass of granite having an outcrop about one mile long and half a mile wide. Presumably the granite cuts across the limestone and ore at a relatively shallow depth. Limestone and tectite are exposed across an area about 1,200 feet wide, and much of this outcrop consists of tectite. Several bodies of ore within the tectite zone



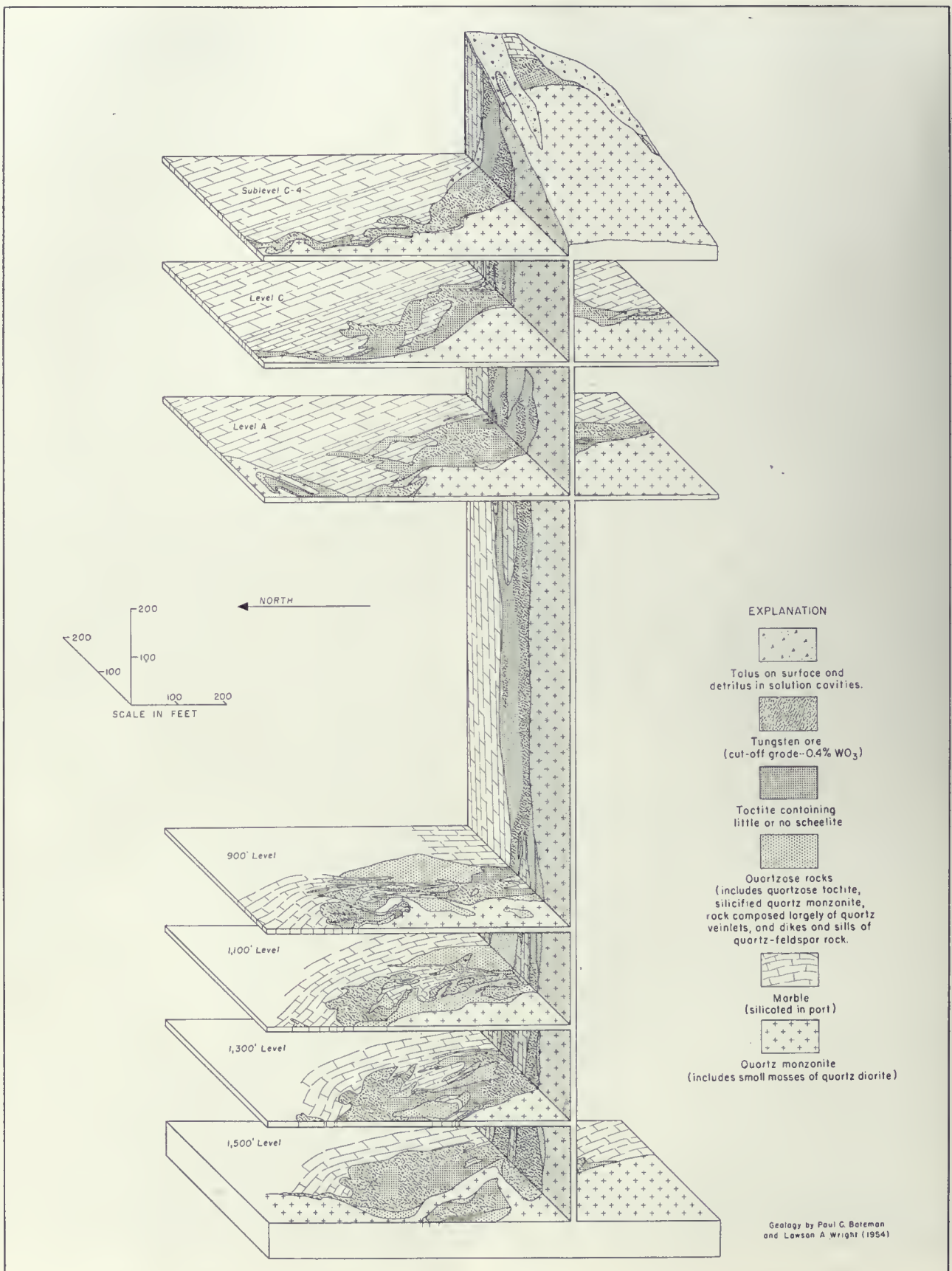


FIGURE 5. Section through the main ore body, Pine Creek tungsten mine. After P. C. Bateman, 1957.





FIGURE 6. Black Rock tungsten mine, Benton Range, Mono County; mine workings in center, mill at extreme right center, Sierra Nevada in background. Photo by Symons Flying Service, Bishop. *Courtesy of Wah Chang Mining Corporation.*

have been explored by open pits and underground workings on four levels. The deposit is being mined by the Wah Chang Mining Corporation, and production early in 1956 was at the rate of 700 tons per day. (*Western Mining and Industrial News*, 1956, vol. 24, no. 2, p. 8.) The ore is treated in an all-flotation plant.

Contact-metamorphic deposits in other areas that have supplied important amounts of tungsten ore include several deposits in the Darwin district in Inyo County (Bateman and Irwin, 1954, p. 34), the Consolidated, Tungstore, and Tulare County mines in Tulare County (Krauskopf, 1953, pp. 14-17), the Garnet Dike mine in Fresno County (Krauskopf, 1953, pp. 13-14), the Strawberry mine in Madera County (Krauskopf, 1953, pp. 9-12), and the Starbright mine north of Barstow in San Bernardino County (Bateman and Irwin, 1954, pp. 35-36). The last, discovered in 1950, is of particular interest because it lies in a district where tungsten production previously had been small.

Areas from which relatively small amounts of tungsten ore have been produced include the upper Kings River

area in Fresno County and the area between the upper reaches of the San Joaquin and Fresno Rivers in Madera County (Krauskopf, 1953); the New York and Old Woman Mountains in San Bernardino County (Bateman and Irwin, 1954, pp. 36, 38; Wright, et al., 1953, p. 148); and the Kernville and Welden districts in Kern County. The deposits of all these areas, except those in the New York Mountains, are scheelite-bearing contact-metamorphic bodies. In the New York Mountains, wolframite and huebnerite are disseminated in pegmatite dikes and quartz veins. Scheelite concentrations occur in the Idaho-Maryland mine, Nevada County, and small amounts of ore were being mined early in 1956. Scheelite previously had been recovered from tailings at the mine.

*History of Production.* The first commercial tungsten production in California was obtained in 1905 from the Stringer district in eastern Kern County. With the discovery of the Atolia district shortly afterward, California became an important source of tungsten. At this time, the ferberite deposits in Colorado were the nation's



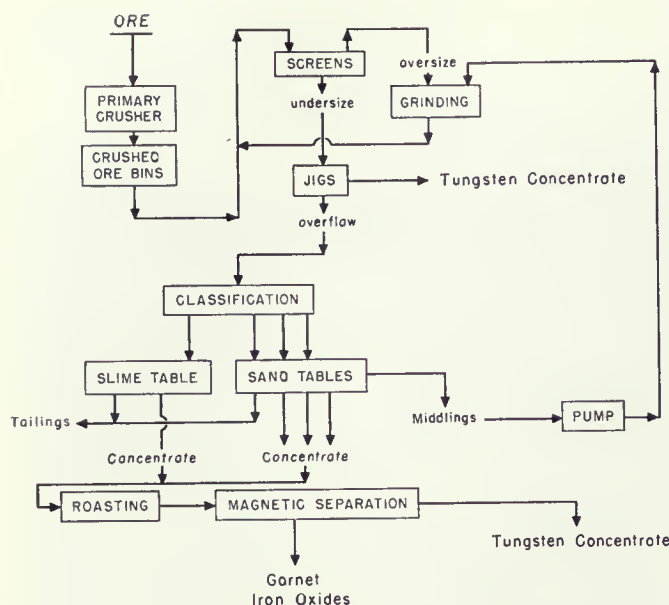


FIGURE 7. Generalized flowsheet of small tungsten mill.

principal tungsten source, but in 1915, largely as a result of production from the Atolia district, California's tungsten output exceeded Colorado's.

The tungsten deposit of the Bishop district had been discovered by 1913, but the first recorded production was obtained in 1916. By 1918 several mines in this district were operating.

The peak production of this early period was reached in 1917 when a total of 2,466 tons of concentrates was obtained. After the war, prices fell and tungsten output slumped. During the period 1921-22 no tungsten was produced in the state. In 1922, when an import duty was levied on tungsten, production was resumed.

California's tungsten output increased to 781 tons of concentrates in 1924 and then declined until 1933. Except for a minor slump in 1935, production increased from 1933-43. In 1937 this increase was spurred by an increase in price, brought about by the rearmament program. It reached a high of 4,235 tons of concentrates in 1943. In the period 1943-47 production dipped sharply, but prices have continued high and in 1948 there was a marked upswing to 1,767 tons of concentrates for the year.

A decrease to 952 tons in 1949 reflected production problems at the Pine Creek mine. World-wide scarcity and government encouragement of domestic production caused a sharp upswing in the production starting in 1950. In 1954, sources in California yielded 3,512 short tons. Because of the continuing government price support for tungsten concentrates from domestic sources, production continued at a high rate through 1955. Production in 1956 declined because of the completion of one stockpile program and the lag in initiating another program that finally had to be discontinued late in the year pending the appropriation of more funds.

**Mining.** Tungsten deposits are mined in much the same way as deposits of other metals. Some ore is obtained from open cuts, but most is mined from underground workings. Mining methods range from simple

open stoping yielding low tonnages to large-scale, sub-level, blast-hole stoping as employed at the Pine Creek mine (McKinley, 1951, pp. 79, 80; Bateman, 1956).

In the upper part, the "old mine," of the Pine Creek mine, some shrinkage stopes were used, but all ore is now obtained from a sub-level stoping system in workings connected to the low-level adit, the Zero level. In ore bodies as wide as 20 to 40 feet, sub-level drifts are driven at 40-foot vertical intervals above a haulage level and in opposite directions from a central raise. Each drift may be as long as 150 feet and connects with a raise at the end of the block of ore that may be as high as 200 feet. Each end raise is widened to a slot across the entire width of the ore body. Diamond drill blast holes are then ring drilled—the holes having angular spacing in one plane—from the sub-level drifts, starting at the slots and retreating toward the central raise. The rings of holes cover a vertical angle of at least 90° and are spaced at intervals of 5 feet. Several rings are blasted in sequence, using millisecond delays. The sub-level nearest the haulage level is started first, and the others follow in sequence.

In ore bodies less than 20 feet wide, sub-level drifts are driven along one wall at 50-foot vertical intervals and connect to raises as above. The drifts are then widened to the limits of the ore body, and slots are cut from the end raises. Rows of long vertical holes are drilled across the ore body from the sub-levels at 7-foot centers. The rows of holes are blasted in pairs.

At Atolia (Wright et al., 1953, p. 145), the methods employed in mining the placer deposits are notable in that as much as 90 feet of overburden was removed to reach channels of scheelite-bearing gravel 8 to 9 feet thick. Open cuts also are used to mine the surface portions of some of the veins in the weathered quartz monzonite. Weathering has extended to depths of 50 to 100 feet, and the rock is easily broken. Cuts ordinarily are 100 to 200 feet wide and 30 to 60 feet deep.

One unique aspect of mining scheelite-bearing deposits is the use of the ultra-violet light. It is not only an invaluable tool during the prospecting stage, but once the occurrence and distribution of the scheelite is understood, the ultra-violet light is valuable as an aid in controlling the grade of ore mined.

**Milling.** The high specific gravity of tungsten minerals, ranging from approximately 6 for scheelite to 7.2-7.5 for the wolframite series, makes them amenable to gravity concentration methods, which are the most widely used in the industry. The chief difficulty in this method is the loss of tungsten minerals in the fine sizes (slimes). Tungsten minerals are very friable and brittle, and unless their recovery is effected as soon as they are free, they will be over-ground, and slime losses will occur. These losses may be so high as to make an operation uneconomical.

Prevention of overgrinding of the ore minerals may be accomplished by stage crushing in closed circuit with screens and the use of jigs either between the grinding unit and classifier in closed circuit, or just ahead of the grinding-classifier circuit.

Concentrating tables are standard equipment in almost all tungsten mills. Adequate hydraulic classification of the table feed adds considerably to table efficiency. Flotation is a very important method in treating com-



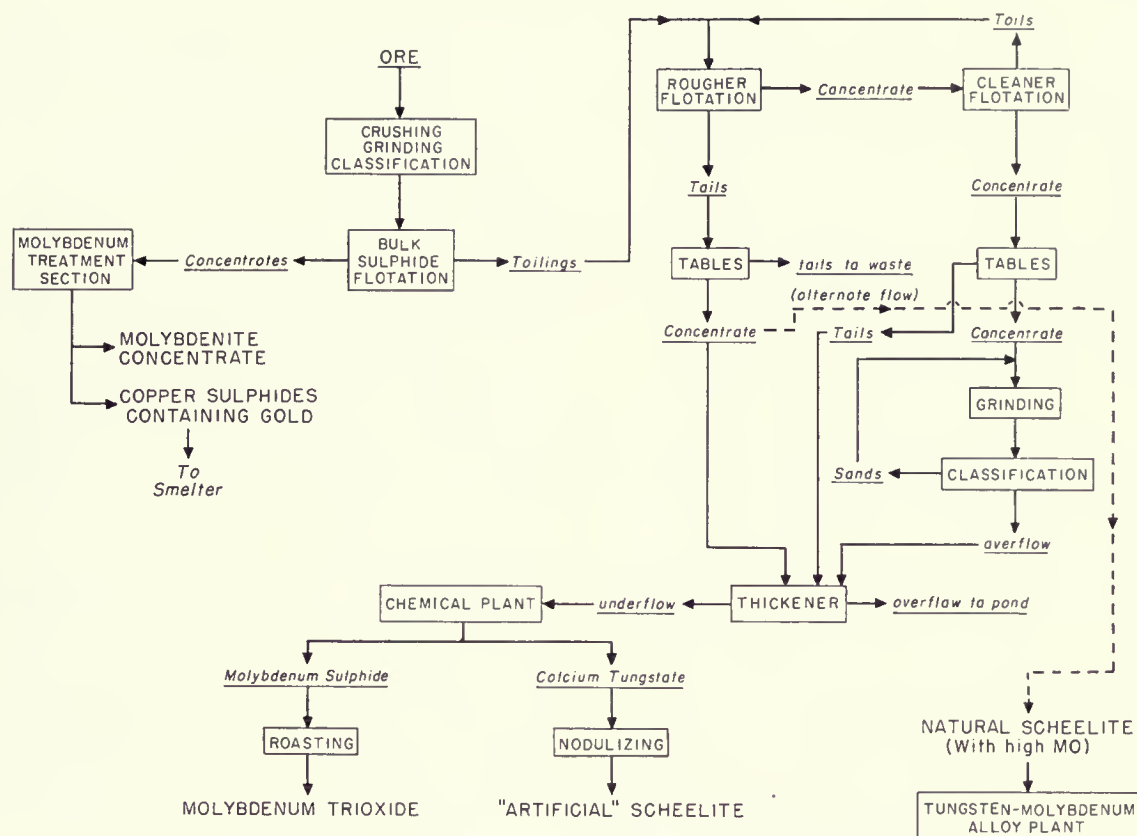


FIGURE 8. Generalized flowsheet of Pine Creek mill, Inyo County.

plex ores, especially those containing sulfide minerals, and in recovering "slimed" tungsten minerals. Owing to the presence of such minerals as fluorite or calcite that are concentrated with scheelite in the flotation process, a flotation concentrate may be too low-grade to be shipped direct. Subsequent treatment may involve table concentration and chemical digestion. Garnet and sulfide minerals, which are both common in scheelite deposits, must be removed by a flotation process, as they otherwise become concentrated with scheelite and have to be removed by roasting and magnetic separation.

In the mills that employ only gravity concentration methods, recovery may average from 60 to 70 percent; an 80 percent recovery is exceptional. The use of flotation in conjunction with gravity methods may permit recoveries as high as 70 to 90 percent (Geehan, 1955, pp. 3, 4).

Figure 7 shows a generalized flowsheet of a typical small tungsten mill. By way of contrast, figure 8 summarizes the Pine Creek milling operation. The notable feature of the Pine Creek mill is the chemical section wherein tungsten and molybdenum are recovered in high-grade marketable products.

A milling problem is faced by operators of most small tungsten mines because the tungsten sold to consumers or to the government stockpile must be in the form of a concentrate containing at least 60 percent  $WO_3$ . Tungsten ore is rarely this rich, so the producer has three choices: (1) sell his ore to a mill operator, (2) have his ore custom milled and market the concentrates himself, or (3) mill the ore himself. In determining the best

possible course of action, the mine operator should consider these factors:

- (1) Size and grade of deposit. These factors determine the gross value of the ore. Grade may be considered by itself if existing mill facilities are to be utilized. Grade and size—the gross value—bear importantly on whether or not a mill can be constructed profitably.
- (2) Nature of the deposit. Is the ore amenable to ordinary methods of concentration that will produce a marketable concentrate without expensive losses?
- (3) Location of deposit. This alone may dictate the outlet for the ore.
- (4) Availability of water, supplies and labor at reasonable cost.

If these factors rule out the advisability of constructing a mill, the other two choices should be compared on the basis of probable net returns. Operators of custom mills charge in the range of \$8 to \$15 per ton of tungsten ore milled. The price schedule that was in effect in September 1956 at the only continuing ore-buying facility in California is shown below (McKinley, H. L., Union Carbide Nuclear Corporation, personal communication). This is not a rigid schedule, but it can be considered typical for the grades and types of ores being purchased by this company in 1956. Other prices might be arranged by the company, depending upon laboratory tests and amounts of ore offered.

A calculation would show that 100 tons of ore containing 0.60 percent  $WO_3$  would be worth \$1,740 if sold to this ore-buying facility. In comparison, if 100 tons of ore of this same grade was treated at a custom mill



Grade of ore (% WO <sub>3</sub> )	Grade of concentrate or ore (% WO <sub>3</sub> )	Price (dollars per short ton unit of WO <sub>3</sub> )
0.00-0.399 inclusive	-----	No payment
0.40-0.449 "	-----	27.00
0.45-0.499 "	-----	27.75
0.50-0.549 "	-----	28.25
0.55-0.599 "	-----	28.75
0.60-0.649 "	-----	29.00
0.65-0.699 "	-----	29.25
0.70-0.749 "	-----	29.50
0.75-0.799 "	-----	29.75
0.80 and higher	-----	30.00
	5.00-7.499 inclusive	31.00
	7.50-9.999 "	32.00
	10.00-14.999 "	33.00
	plus steps to	
	30.00 and higher	37.00

making only a 60 percent recovery, the concentrates recovered would have a gross value (at the government guaranteed price of \$55 per unit) of \$1,980. After paying a milling charge of \$12 per ton, for example, the net return would be \$780. If the custom mill charged only \$10 per ton of ore milled, and made an 80 percent recovery, the concentrates would have a net value of \$1,640.

Similar calculations can be made for different grades of ore. Thus 100 tons of ore containing 0.90 percent WO<sub>3</sub> would be worth \$2,700 at the ore-buying facility; the mill that was 80 percent efficient and charged \$10 per ton would recover concentrates having a net value of \$2,960; the mill that was 60 percent efficient and charged \$10 per ton would recover concentrates having a net value of \$1,970.

Custom mills at numerous places in California have operated from time to time, but most of these operations have not been continuous over long periods. Concentrates recovered at these mills have been sold to local buyers or to the government for the stockpile. In California, the General Services Administration handles the purchase of domestic tungsten concentrates through the office of the Defense Materials Service at 49 Fourth Street, San Francisco 3. Purchases by this agency are dependent upon the existence of an authorized program. Refer to the section on Government Programs, later in this report.

**Metallurgy.** Although some high-purity scheelite concentrates are charged directly into furnaces to make

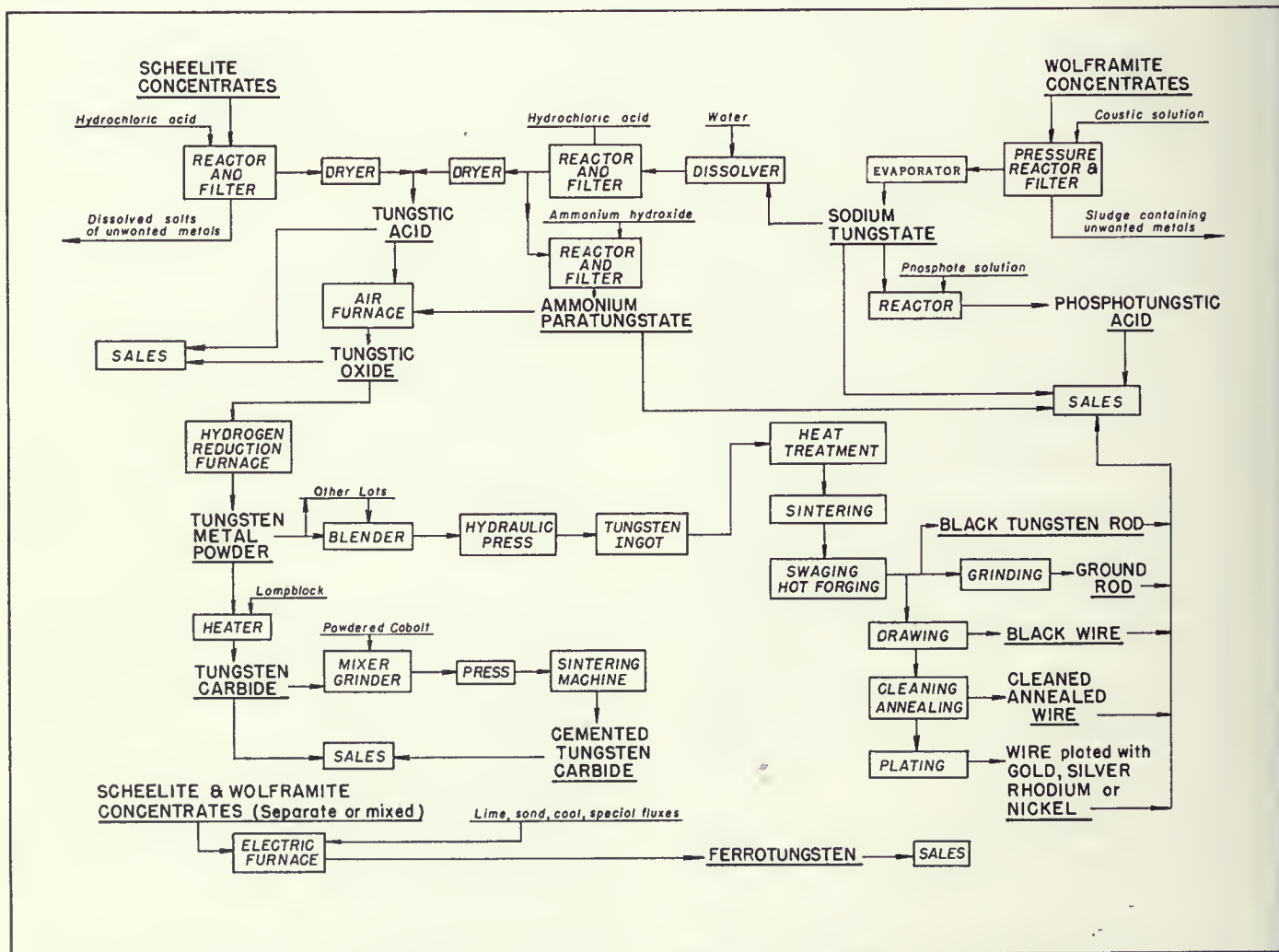


FIGURE 9. Preparation of tungsten compounds and tungsten metal products. Adapted from C. R. Hayward, 1952; K. C. Li and C. U. Wang, 1955; Sylvania, 1954; and L. F. Yntema, 1954.



alloy steel, most tungsten concentrates are subjected to metallurgical processes to produce pure tungsten powder or ferrotungsten. Tungsten powder in turn is processed further to make tungsten metal in various forms or tungsten carbide, the hardest artificial substance in common use.

The extractive metallurgical treatment of tungsten concentrates consists of four steps: (1) decomposition of the ore, (2) preparation of a pure or hydrated oxide, (3) reduction to metal powder, and (4) conversion of the powder to massive metal (Yntema, 1954, p. 485). The various steps are complex, carefully controlled, and yield intermediate marketable products such as sodium tungstate, phosphotungstic acid, tungstic acid, ammonium paratungstate, and tungstic oxide. Figure 6 outlines the preparation of these compounds and metal products. The reduction of the tungstic oxide is a batch process wherein control is carefully exercised over the flow of hydrogen, the temperatures involved (1300° F. to 1900° F.) and the time of reduction. These factors influence the particle size of the resulting tungsten powder; particle sizes that range from 0.5 to 5.0 microns give optimum results in the further preparation of the massive metal.

The melting point of tungsten, which is approximately 3400° C. (6152° F.), is the highest of any metal and of any element except carbon (Yntema, 1954, p. 483). Powder metallurgy techniques were developed originally to produce tungsten in a usable form. Tungsten rod is prepared by pressing blended lots of tungsten powder into small ingots. These are treated in two stages, at temperatures of approximately 2200° F. and 5500° F. The ingot then can be swaged at elevated temperatures to produce rod, which can be further swaged and drawn at high temperatures to produce wire and filament. This hot drawing must be at temperatures below the recrystallization temperature for tungsten, or about 1500° C.

Powder-metallurgy is also used to produce cemented tungsten carbide. Tungsten carbide powder is mixed with powdered cobalt, pressed into small bars and sintered in a reducing atmosphere.

Ferrotungsten is prepared from tungsten powder by a thermite process, either aluminothermic or silicothermic, or by electric furnace methods. Ferrotungsten can also be prepared directly from high-grade ferberite concentrates by carbon reduction with suitable fluxes. According to Wang (1951, p. 856) there is a trend toward an increasing use of high-purity tungsten concentrates and a decreasing use of ferrotungsten in the manufacture of high-speed tungsten steel.

**Utilization.** The properties of tungsten that make it so useful in modern technology include a melting point, 3400° C. (6152° F.), higher than any other metal; a low vapor pressure; an electrical conductivity about one-third that of copper; an expansion coefficient about one-fourth that of copper; a density about 2½ times that of steel and twice that of lead; a high tensile strength and elasticity; and, possibly most important, retention of much of its tensile strength and elasticity at temperatures of 500° C. and over.

The use pattern of tungsten is influenced by two factors that have become apparent during the period 1942-55:

1. During periods of actual tungsten scarcity, consumers were encouraged to design tungsten out of their products. This trend is believed by many to be unrealistic as "transition from shortage to abundance was the keynote of the tungsten industry during 1953" (Geehan and Burke, 1955, p. 1). In 1953, the Tungsten Institute was formed and its objectives included promotion of the use of tungsten. Late in 1955, this institute arranged for a research program to develop new high-tungsten alloys for high temperature applications.

2. Tungsten carbide has become the most important tungsten-consuming product. Tungsten powder is the raw material from which tungsten carbide is produced. The growth of this industry is indicated in the table below.

*Consumption of tungsten concentrates*

Year	Steel ingots and ferrotungsten (percent)	Metal powder and other (percent)
1942	85	15
1943	75	25
1944	72	28
1945	63	37
1946	63	37
1947	63	37
1948	64	36
1949	63	37
1950	45	55
1951	30	70
1952	24	76
1953	37	63

As can be seen, prior to 1950, tungsten was used principally in the manufacture of alloy steels, particularly the "high-speed" steels. Such steels retain their hardness even at red heat and will remain sharper and can take a heavier cut than tools of ordinary carbon steel. With "high-speed" tools, the output per man and machine was increased about five-fold. The original "high-speed" steel, which is known as the "18-4-1" type, contains 18 percent tungsten, 4 percent chromium and 1 percent vanadium, plus 0.65 to 0.75 percent carbon. A series of tungsten-cobalt steels, containing from 5 to 12 percent cobalt, and stellite, a nonferrous cobalt-chromium-tungsten alloy, are also used for high speed cutting tools.

The most important use for tungsten products continues to be in tools used to cut or machine steel. However, tungsten carbide has become increasingly important in this field. It is the hardest artificial substance in common use, and, in addition to its use in cutting tools, it is used as inserts in rock bits, in dies for drawing tungsten wire and in welding electrodes used for hard-facing machinery parts. Tungsten carbide may be combined with carbides of other metals, principally tantalum and titanium.

Tungsten steels are used for a wide range of products, including hacksaw blades, cold chisels, razor and knife blades, armor plate, armor-piercing projectiles, drawing dies for wire manufacture, valve seats, and rails. Copper-tungsten and silver-tungsten alloys are used for welding electrodes and electrical contacts.

Tungsten in rod, wire, or disc form, is one of the few metals used commercially in a very pure state. Such industrial tungsten usually has a purity of 99.95 percent plus, although minute amounts of impurities are added for special applications. Because of its high melting point (3400° C.), low vapor pressure, high tensile strength, and ductility, tungsten is used as filaments for incandescent electric lamps and radio tubes. Filament wire sizes range from 0.060 to 0.0003 inch in diameter.



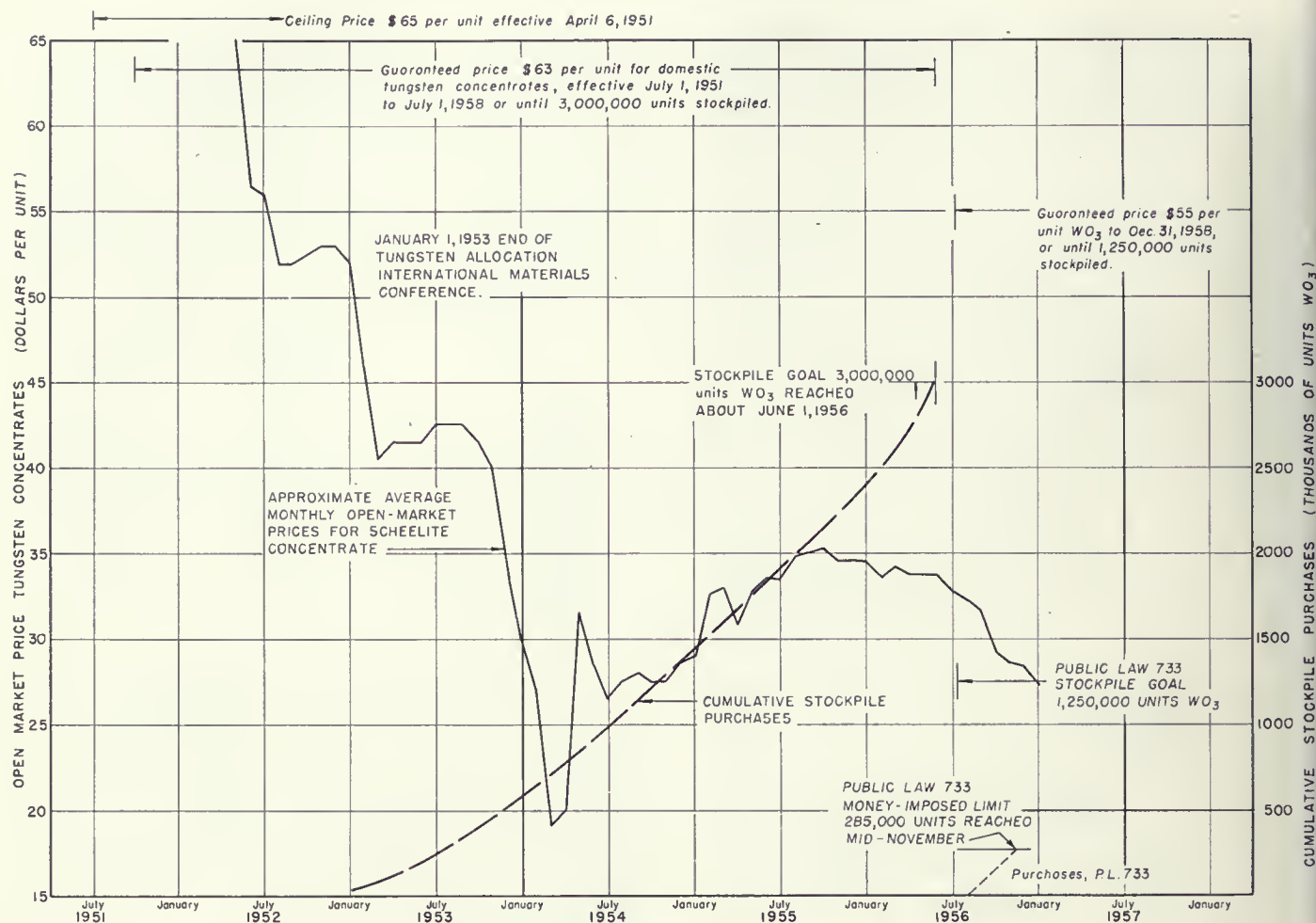


FIGURE 10. Tungsten market factors, 1951-1958.

One pound of tungsten can be drawn into nearly 8.5 miles of filament having a diameter of 0.00183 inch; this would provide filaments for 23,000 60-watt lamps (Wang, 1951, p. 854). Though relatively small amounts of tungsten are consumed in the manufacture of filaments, no adequate substitute has been found for it in this use.

Tungsten is utilized in various chemical compounds, in dyes and paints, in fluorescent materials for x-ray photography, and in coloring agents in the manufacture of porcelains and stained papers.

**Government Programs.** China has been the world's principal source of tungsten ore, and the potential there is emphasized by the following statement (Wang, 1951, p. 856): "With regard to tungsten production in the different countries, the following figures are given as indicative of their potentiality in production: taking Russia as a unit, China's potentiality is 90, Korea 4.3, United States 4, Burma 4, Brazil 2.2, Bolivia 2, Tasmania 1, Portugal 1, Russia 1, and the rest of the world taken together 2.3." It is not surprising then that the world tungsten market during the period 1950 through 1952 was dominated largely by the loss of China, through Communist control, as a source of tungsten ore for the free world. Also the Korean war caused an increased

demand for tungsten, and the world-wide attempts to obtain sufficient supplies became sharply competitive.

From mid-1951 to December 31, 1952, as a remedial measure, tungsten was allocated, by the International Materials Conference, to the participating countries (11 altogether, including the United States and the United Kingdom). Quotas were based on estimates of production and consumption submitted every three months by the producing and consuming countries. Quotas were terminated at the end of this period, because emergency measures had led to a 50 percent increase in the production of tungsten in the free world. Much of this increase was caused by a successful expansion of the output from South Korea's mines. By trade agreement, all of this output was exported to the United States. In 1952 and 1953, South Korea led all other nations in the shipment of tungsten concentrates to the United States.

Recognizing the importance of a domestic tungsten mining industry, the government has taken steps to encourage the exploration for and exploitation of tungsten deposits. The Defense Production Act of 1950 authorized the establishment of an assistance program for the exploration for mineral deposits. This program, implemented by the Defense Minerals Exploration Agency (DMEA), included tungsten in the group of commodities



for which the government would provide loans covering 75 percent of the cost of approved exploration projects.

Through July 1955, seventeen contracts had been negotiated for tungsten exploration projects in California. The total cost of these projects was \$581,037, and the government's share was \$435,777.50 (Ricker, S., Executive Officer, DMEA Field Team, Region II, personal communications, 1954 and 1955). Nearly 38 percent of all applications for exploration loans in California have been made on tungsten properties, and contracts awarded on tungsten properties represent 38 percent of all contracts in California.

Owing to the shortage of tungsten on the world market, domestic prices rose from an average value of \$25.36 per unit of  $WO_3$  for the period 1947-49 inclusive to \$47 at the end of 1950. A price of \$65 was reached by late January 1951. On April 6, 1951, a ceiling price of \$65 per unit of  $WO_3$  was established by the Office of Price Stabilization. At about the same time, the Defense Minerals Administration announced that the price for domestic tungsten concentrates purchased for the government stockpile would not fall below \$63 per unit. By way of contrast, the price established by the Metals Reserve Company during World War II was just \$30 per unit.

Congressional action authorized the General Services Administration to start a program on July 1, 1951 for the purchase of domestic tungsten concentrates containing a minimum of 60 percent  $WO_3$  at a guaranteed price of \$63 per unit. This program was to be in effect for 5 years or until 3,000,000 units had been purchased. In August 1953, the program was extended by Congress until July 1, 1958 or until the unit goal is reached, if that is sooner.

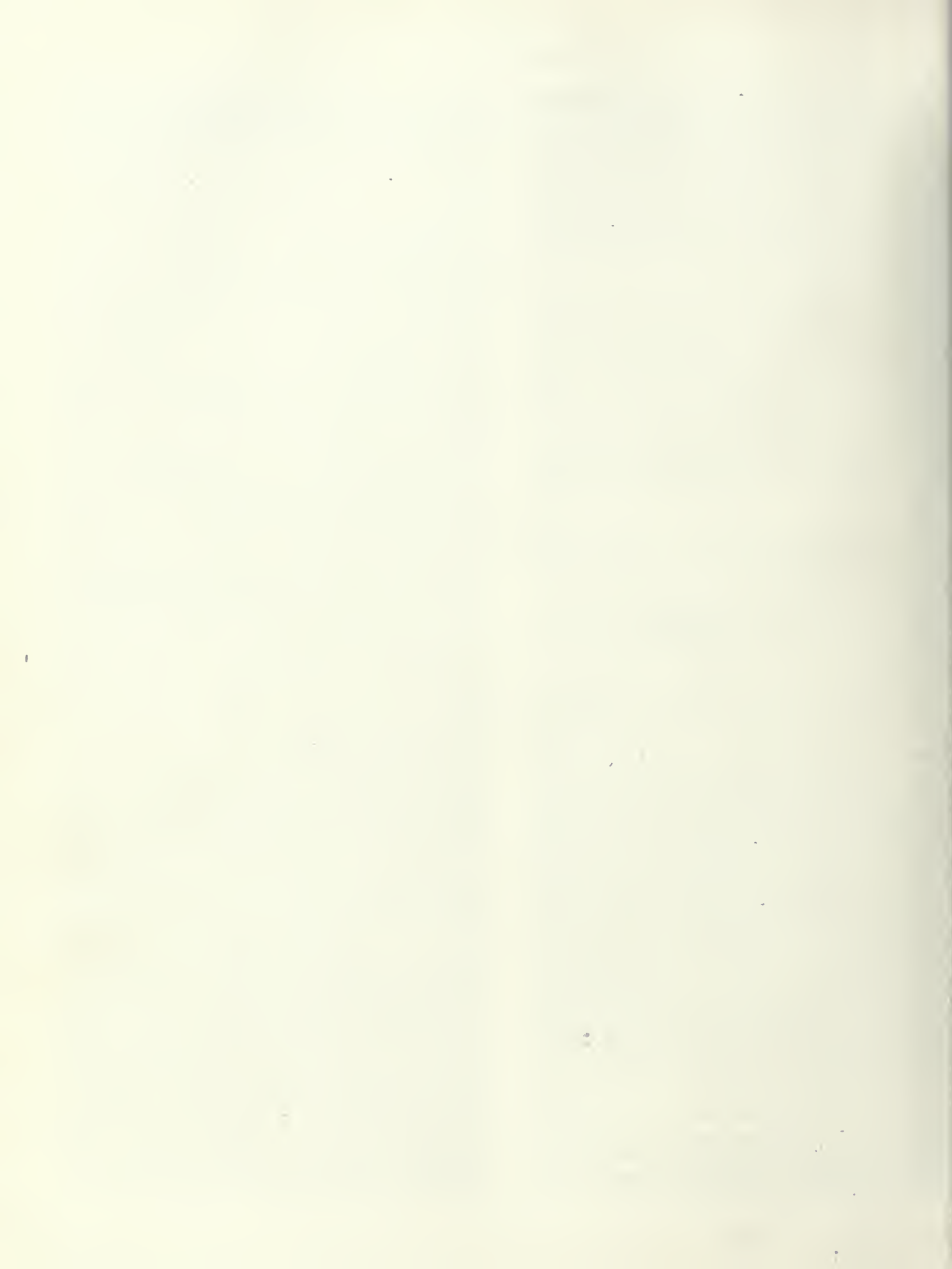
Deliveries of tungsten concentrates to the government stockpile were slow during the early part of the program, owing to a high open-market price. However, from mid-1952 to early in 1954, this price dropped from \$55 to \$20 per unit, and concentrates were sold to the stockpile at an increasing rate. Thus the amount of concentrates held by the stockpile was more than doubled during the last half of 1953. Figure 7 shows open market prices and portrays government stockpile programs through 1956. During 1955, it became clear that if deliveries continued at current rates, the 3,000,000 unit stockpile limit would be reached in mid-1956. This goal was reached and the program terminated early in June, 1956.

Public Law 733, cited as the *Domestic Tungsten, Asbestos, Fluorspar, and Columbium-Tantalum Production and Purchase Act of 1956*, was passed and approved on July 19, 1956. The program thus established provided for the purchase of 1,250,000 short ton units of  $WO_3$  contained in domestic concentrates at a price of \$55 per unit. However, Congress appropriated enough funds to purchase only about 285,000 units. Purchasing was started in mid-August and was discontinued in mid-November, pending the appropriation of more funds to carry on the program.

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## URANIUM

BY BENNIE W. TROXEL, MELVIN C. STINSON, AND  
CHARLES W. CHESTERMAN

The search for uranium as a source of atomic energy has led to an unprecedented interest in prospecting in California and to the discovery of radioactive minerals at 200 to 300 localities within the state. The deposits lie mainly in the arid parts of the state, particularly in the desert region of southern California.

The total production of uranium in California is very small to date, and only a few of the discoveries appear to be of present economic interest. By 1956, only a few hundred tons of ore had been shipped, and this was obtained mostly from six mines. Uranium deposits that are of subcommercial grade at present have been discovered in several places in the state and may be worked in the future.

The only uranium mill in California to date was built in 1955 near Mojave. It was intended to treat ore from a property near Rosamond, but operated only for a few months during the latter part of 1955 and early 1956. No uranium concentrates were sold.

**Mineralogy.** Uranium combines with other elements to form a large variety of minerals of which relatively few are sufficiently abundant to be of commercial value. Uraninite, pitchblende, and davidite are the most common of primary uranium minerals and generally occur in veins of hydrothermal origin. In California the most abundant secondary minerals are carnotite, autunite, tyuyamunite, torbernite, uranophane, and schroeckingerite. Primary uranium mineral grains commonly are surrounded by "halos" of yellow or orange gummite or other secondary uranium minerals.

Uraninite and pitchblende are mixtures of  $\text{UO}_2$  and  $\text{UO}_3$  with various proportions of radium, lead, combined rare earths, thorium, and helium. The term "uraninite" is generally used for material with a definite crystal habit, usually cubic, and "pitchblende" for the massive or amorphous varieties. Both have a steely to velvety black, brownish-black, gray or greenish color, a submetallic to pitch-like, greasy, or dull luster, and a brownish-black, gray to olive-green streak. Their specific gravity ranges from 6.5 to about 10.5. Uraninite and pitchblende are infusible or slightly rounded on edges of thin splinters when heated before a blowpipe.

Two minerals—allanite and samarskite—may be mistaken for uraninite or pitchblende. Both allanite and samarskite are common in pegmatites. Allanite is easily fusible to a black magnetic bead. Samarskite, compared with uraninite or pitchblende, has a low specific gravity (5.4 to 5.7). Before a blowpipe, samarskite glows, cracks open, turns black, and fuses on thin edges to a black glass.

Davidite, a mixture of rare earth-iron-titanium oxide and uranium oxide is characterized by a dark brown to black color, glassy to submetallic luster, hardness of 5 to 6, and a specific gravity of 4.5. It generally occurs in irregular masses.

Nearly all of the secondary uranium minerals are characterized by brilliant colors, particularly yellow, orange, or pale green. Some of them are brilliantly

fluorescent under ultra-violet rays. Most of them are soft and powdery.

Carnotite ( $\text{K}_2\text{O} \cdot 2\text{UO}_3 \cdot \text{V}_2\text{O}_5 \cdot 1.3\text{H}_2\text{O}$ ) is canary yellow with a dull or earthy luster, if massive; or a pearly luster if coarsely crystalline. It occurs as aggregates and inclusions.

Tyuyamunite ( $\text{CaO} \cdot 2\text{UO}_3 \cdot \text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ ) is pale greenish-yellow, and has physical properties similar to carnotite except that it commonly has a weak yellow-green fluorescence whereas carnotite is non-fluorescent. It is present in small amounts in most occurrences of carnotite, and is the principal mineral in some uranium deposits.

Carnotite and tyuyamunite can be distinguished from other yellow non-fluorescent or weakly fluorescent uranium minerals by the presence of vanadium, which causes samples to turn red-brown when touched with a drop of concentrated hydrochloric or nitric acid. Carnotite is soluble in all acids including acetic acid and is infusible in the blowpipe flame. Tyuyamunite, on the other hand, is not soluble in acetic acid and is easily fusible to a dark melt.

Autunite ( $\text{CaO} \cdot 2\text{UO}_3 \cdot \text{P}_2\text{O}_5 \cdot 12\text{H}_2\text{O}$ ) and meta-autunite ( $\text{CaO} \cdot 2\text{UO}_3 \cdot \text{P}_2\text{O}_5 \cdot 8\text{H}_2\text{O}$ ) are lemon-yellow to apple-green, have pearly to sub-adamantine luster, and a specific gravity range of 2 to 3. Both minerals fluoresce brilliant yellow or green on fresh surfaces. They occur most commonly as small tablets with rectangular outlines, or as micaceous masses.

Torbernite ( $\text{CuO} \cdot 2\text{UO}_3 \cdot \text{P}_2\text{O}_5 \cdot 12\text{H}_2\text{O}$ ) and metatorbernite ( $\text{CuO} \cdot 2\text{UO}_3 \cdot \text{P}_2\text{O}_5 \cdot 8\text{H}_2\text{O}$ ) are generally bright emerald-green in color, with pearly to sub-adamantine luster, a specific gravity range of 3.4 to 3.6 and a hardness of 2 to  $2\frac{1}{2}$ . They commonly are faintly fluorescent and occur as square tablets and micaceous masses.

Torbernite and metatorbernite may be mistaken for autunite or meta-autunite because of the similarity in color and habit. Torbernite, however, is weakly fluorescent to non-fluorescent. It most commonly occurs with secondary copper minerals, and will yield chemical tests for copper.

Metazeunerite ( $\text{CuO} \cdot 2\text{UO}_3 \cdot \text{As}_2\text{O}_5 \cdot 8\text{H}_2\text{O}$ ) is grass green to emerald green, has a vitreous to pearly luster, a specific gravity of 3.64, and a hardness of 2 to  $2\frac{1}{2}$ . It occurs in square tablets resembling torbernite. Metazeunerite fluoresces yellow green in ultra-violet light.

Uranophane ( $\text{CaO} \cdot 2\text{UO}_3 \cdot 2\text{SiO}_2 \cdot 6\text{H}_2\text{O}$ ) is lemon-yellow to apple green and occurs as stains or coatings of fibrous or radiating crystals. It has a specific gravity of 3.85 and is locally associated with autunite or carnotite.

Schroeckingerite (approximately  $\text{Ca}_3\text{Na} \cdot \text{UO}_2 \cdot \text{SO}_4 \cdot \text{F} \cdot 10\text{H}_2\text{O}$ ) is yellow to greenish-yellow, has a pearly luster, a specific gravity of 2.5, and a bright yellow-green fluorescence. It occurs as globular coatings on fractures or as small aggregates of flaky crystals in soft rocks or soil. Schroeckingerite is soluble in water and can thus be distinguished from other fluorescent minerals.

The following other secondary minerals have been noted in association with the principal uranium-bearing



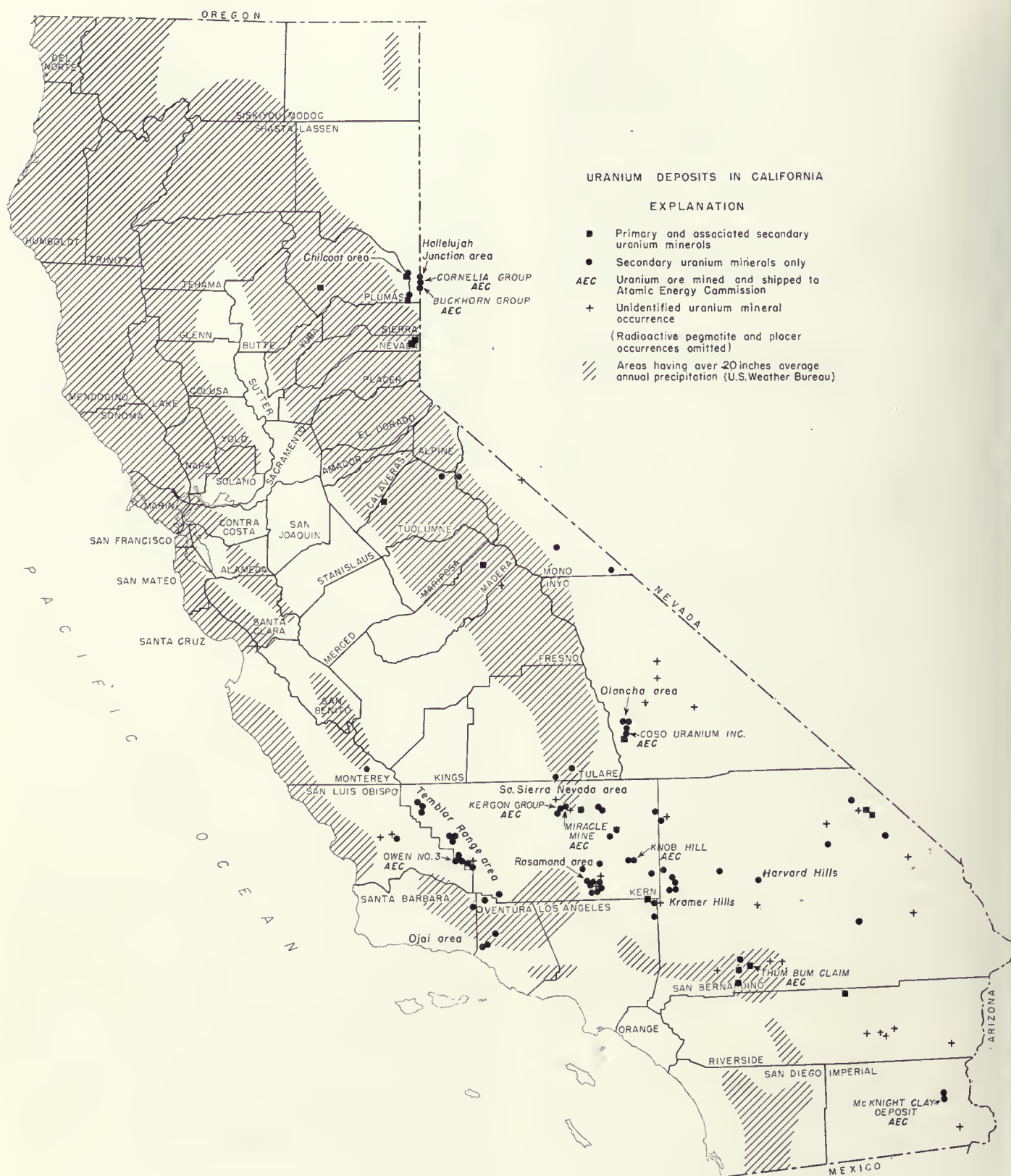


FIGURE 1.



minerals in deposits in California: beta-uranotil,  $\text{CaO} \cdot 2\text{UO}_3 \cdot 2\text{SiO}_2 \cdot 6\text{H}_2\text{O}$ ; euprosklodowskite,  $\text{CuO} \cdot 2\text{UO}_3 \cdot 2\text{SiO}_2 \cdot 6\text{H}_2\text{O}$ ; sabugalite,  $\text{HAl}(\text{UO}_2)_4(\text{PO}_4)_4 \cdot 16\text{H}_2\text{O}$ ; uranocircite,  $\text{Ba}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ ; walpurgite,  $\text{Bi}_4(\text{UO}_2)(\text{AsO}_4)_2\text{O}_4 \cdot 3\text{H}_2\text{O}$ ; and yttracrasite, (?) ( $\text{Y, Th, U, Ca}$ ) $_2\text{Ti}_4\text{O}_{11}$ (?).

**Geologic Occurrence.** Although uranium occurs in rocks of nearly all geologic ages and lithologic types, the principal sources of uranium ores have been (1) hydrothermal veins of primary minerals, or their alteration products, in igneous and metamorphic rocks, and (2) disseminated primary and/or secondary minerals in sedimentary rocks. Uranium also occurs as sparsely disseminated primary mineral grains in igneous rocks; as organo-uranium compounds in coals; with organic matter, pyrite, and phosphatic matter in black shales; in carbonate-fluorapatite in phosphatic beds; and in petroleum and asphalt in sedimentary rocks. In addition to the vein and disseminated deposits, uranium is recovered in the United States from lignite in the north and north-west states, from asphaltic sandstone at Temple Mountain, Utah, and as a byproduct from Tertiary phosphatic rocks in Florida and Permian phosphatic rocks in Idaho, Montana, Utah, and Wyoming.

Hydrothermal vein deposits, the world's principal source of uranium, contain pitchblende or uraninite and various assemblages of silver, cobalt, nickel, lead, and copper minerals. The gangue minerals most commonly consist of one or more of the following: carbonates, barite, quartz, or fluorite. Veins range in width from a fraction of an inch to 15 feet. They occur in fracture zones, fault zones, and intersections of fractures or faults. Most of them are in pre-Cambrian igneous and metamorphic rocks.

Most of the uranium mined in the United States is obtained from disseminated primary and/or secondary uranium minerals in the Colorado Plateau region. Such deposits are principally in terrestrial sandstones, mudstones, and lacustrine limestones of Mesozoic age but some are in similar rocks of Upper Paleozoic and Tertiary age. The deposits range in size from small masses a few inches wide to large masses a few thousand feet in maximum dimension and are as much as 20 feet thick. The average grade of ore from these deposits is probably between 0.2 to 0.4 percent  $\text{U}_3\text{O}_8$ . The well-known occurrences of carnotite in sandstones, and to a lesser extent in mudstones, were probably derived by progressive oxidation of primary black vanadium-uranium minerals (Stocking and Page, 1956, p. 8). The primary minerals replaced or impregnated woody or other carbonaceous material, or occupied intergranular spaces in sandstone.

The principal uranium districts of the Colorado Plateau are on regional structural features but sedimentary features are the dominant local control for individual deposits. The principal sedimentary features are paleostreams, intersections of crossbeds, variations in grain size, and thickened parts of sandstone beds.

Uranium deposits in lacustrine limestone are mined in New Mexico, Arizona, Utah, and Wyoming. The largest deposits of this type are in the Todilto limestone (Jurassic) near Grants, New Mexico. Uraninite, fluorite, and other primary minerals have replaced limestone and have become oxidized to secondary minerals, which fill

joints and vugs and coat bedding surfaces. The deposits occur chiefly along axes of minor anticlines within broad, shallow synclines, which are crudely aligned with major faults (Stocking and Page, 1956, p. 10).

#### LOCALITIES IN CALIFORNIA

Uranium-bearing localities are distributed throughout a large part of California, but most of them are clustered into a few areas in the desert regions of southern California, the southern Sierra Nevada, eastern Plumas County, and southern Lassen County. Many of the localities have been described by Walker, Lovering, and Stephens (1956). Descriptions of deposits in western Kern County and most of the deposits in the southern Sierra Nevada were kindly furnished for this report by W. A. Bowes, U. S. Atomic Energy Commission.

Although most of the uranium-bearing localities in California contain secondary uranium minerals, primary minerals have been noted in a few localities. In some deposits the uranium-bearing minerals have not been identified. The most common secondary uranium minerals in the state are autunite and (meta-autunite), carnotite, torbernite (and metatorbernite), and uranophane. Less commonly occurring secondary minerals are beta-uranotil, euprosklodowskite, gummite, metazeunerite, sabugalite, schroeckingerite, tyuyamunite, uranocircite, walpurgite, and yttracrasite (?). Nearly all of the uranium minerals mined in California to date have been of secondary origin. The first uranium ore to be marketed from California, however, was primary. This was mined from Thum Bum claim near Big Bear Lake, San Bernardino County, and was shipped on July 14, 1954. Since that time at least eight other properties have yielded from 7 tons to several carloads of uranium ore.

**Hallelujah Junction Area, Southern Lassen County.** Three uranium deposits have been found in the low foothills on the west side of the Antelope Range in southern Lassen County, near the California-Nevada border (fig. 1). Fractures that cut Tertiary volcanic and sedimentary rocks contain autunite as the principal uranium mineral. Although a few hundreds of tons of ore was

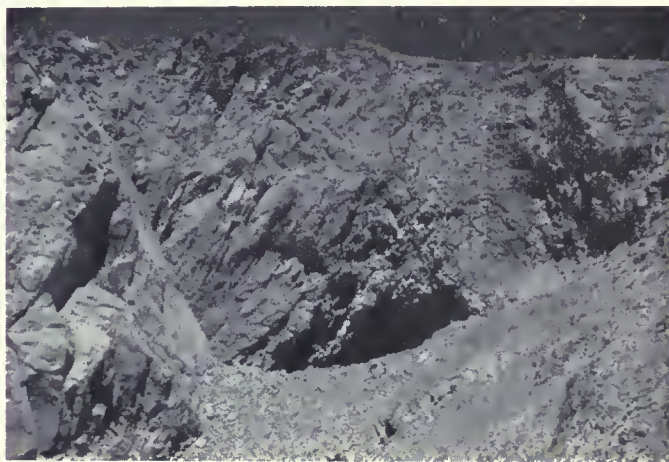


FIGURE 2. View northwest toward open cut on the Cornelia claims near Doyle, Lassen County. Autunite is localized in a north-east-trending vertical shear zone (right side of photo) in sedimentary beds composed of clay, siltstone, sandstone, and conglomerate containing volcanic rock fragments. Shear zone is about 4 feet wide.



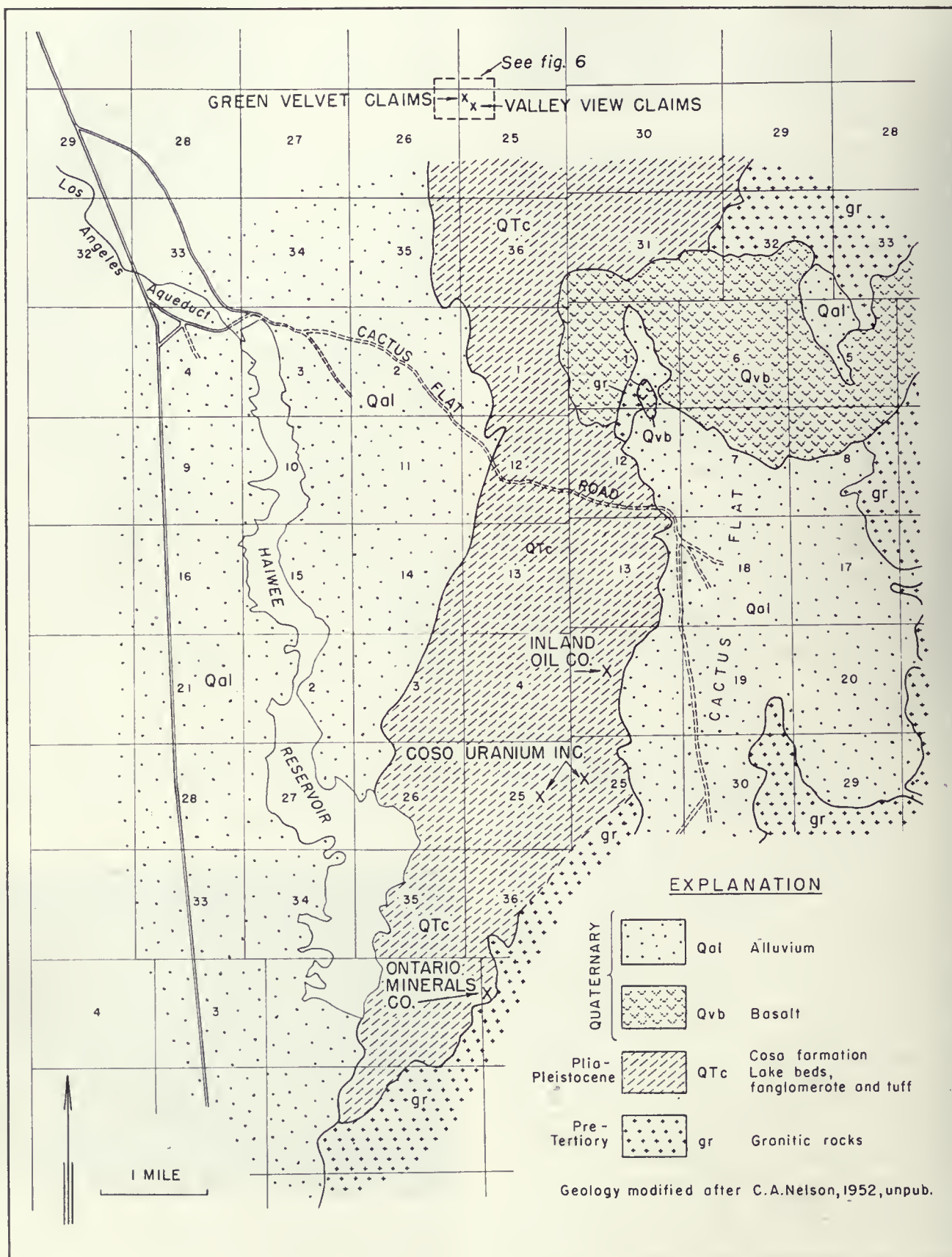


FIGURE 3. Generalized geologic map of Olancha area, Inyo County.





FIGURE 4. Upper adit on property of Coso Uranium, Inc., near Olancho, Inyo County, California. Portal is in granitic rocks which are overlain by gently dipping, uranium-bearing basal arkosic sandstone and conglomerate of the Coso formation.

shipped to the government stockpile at Salt Lake City, Utah, by mid-1955, mining operations were discontinued because the average uranium oxide content of the ore dropped below 0.2 percent. Most of the ore was mined from north-trending, iron-stained seams on the Buckhorn group, and from highly fractured bedded sandstone and clay (fig. 2) on the Cornelia group. At the third deposit, autunite(?) is associated with hydrous iron oxides in cracks and seams in a rhyolite breccia dike. The properties have been developed by several large bulldozer cuts, trenches, a vertical shaft about 75 feet deep, and a 100-foot tunnel.

*Chilcoat Area, Eastern Plumas County.* In June 1954, the dumps of the Mohawk copper mine, 9 miles north of Chilcoat, were found to be slightly radioactive. Subsequent prospecting in the area has led to the discovery of concentrations of secondary uranium minerals—metatorbernite and minor amounts of metazeunerite and cuprosklodowskite—in quartz veins and shear zones in decomposed granitic rock. Although three uranium-bearing localities are known in this area, no ore has been shipped from them to date (1956).

*Olancho Area, Inyo County.* Secondary uranium minerals have been noted in the Coso formation (Plio-

Pleistocene) in several locations along the east side of Owens Valley, within 12 miles southeast and east of Olancho, Inyo County. The Coso formation, which underlies several square miles on the west and northwest flanks of the Coso Range, is composed principally of moderately coarse to fine-grained arkosic sandstone and tuffaceous and bentonitic lake beds which lie upon an irregular surface developed on Jurassic granitic rocks. The sedimentary rocks, capped in large part by volcanic flows, strike approximately north and dip gently to the west, but locally are warped into broad, shallow folds.

From south to north, the four most extensively developed properties are those of Ontario Minerals Company, Coso Uranium, Inc., Inland Oil Company, and the Green Velvet and Valley View claims (fig. 3). At the property of Ontario Minerals Company, radioactive minerals occur in lenses of dark gray (opaline ?) material along an east-trending fault that separates granitic rocks on the south from rocks of the Coso formation on the north. At this locality, uranium mineralization also has been noted in the matrix of arkosic sandstone at the base of the Coso formation. Hand-selected material containing 0.2 percent  $U_3O_8$  or more has been mined from a short adit, but none has been shipped to date (1956).





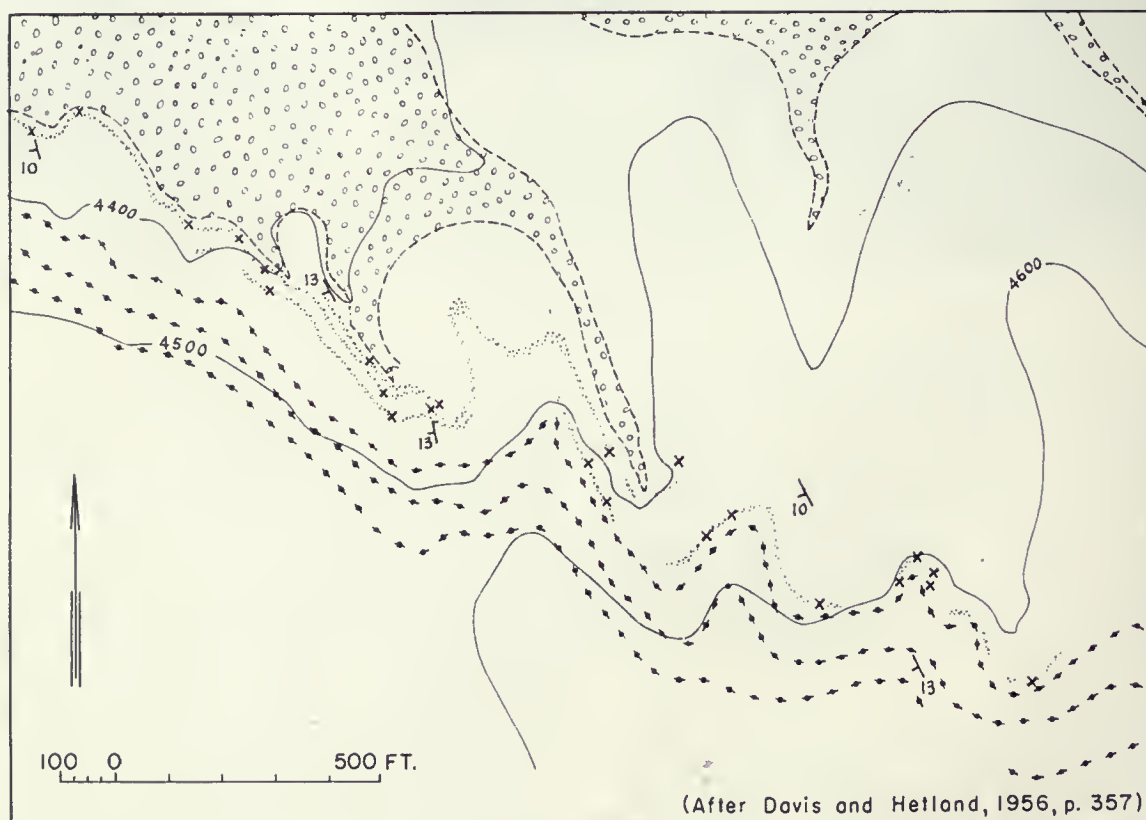
FIGURE 5. View west toward large open cut in sandstone and bentonitic volcanic ash of the Plio-Pleistocene Coso formation on the Green Velvet claims, Inyo County. Beds dip gently into hill. Uranium minerals are localized in friable sandstone near feet of boy.

At the property of Coso Uranium, Inc., poorly cemented arkosic sandstone and conglomerate at the base of the Coso formation contain uranophane and autu-

nite in iron-stained bedding planes and fractures. By mid-1956, the property had been developed by five adits, an inclined shaft, and several open cuts and trenches (fig. 4). Approximately 300 tons of low-grade uranium ore was shipped to Vitro Uranium Company, Salt Lake City, Utah.

At the Inland Oil Company property, autunite has formed along bedding planes and fractures in multi-colored bentonitic clay beds which are about 2 feet thick and lie several tens of feet stratigraphically above the base of the Coso formation. Although these beds are traceable for at least a mile along the surface, they are only locally radioactive and by mid-1956 no ore had been shipped.


The Green Velvet and Valley View claims (figs. 5 and 6) contain autunite and radioactive opal in tiny fractures (Davis and Hetland, 1956, p. 358) in bentonitic clays and fine-grained, poorly-cemented sandstone of the Coso formation. These deposits appear to lie a few hundred feet above the base of the formation. Three uranium-bearing, iron-oxide stained beds, 8 to 24 inches thick, persist along strike for about 2,000 feet (Davis and Hetland, 1956, p. 358). Small pods within these beds contain 0.2 percent or more  $U_3O_8$ , but none has been shipped to date (1956). Exploration has been by bulldozer cuts, shallow trenches, and small open pits.



 Alluvium

 Arkosic sandstone and caliche beds

 Location of uranium minerals

Plio  Coso formation  
Pleist (lake beds)


 Iron-stained zones

FIGURE 6. Geologic map of the area around the Green Velvet and Valley View claims near Olancha, Inyo County.



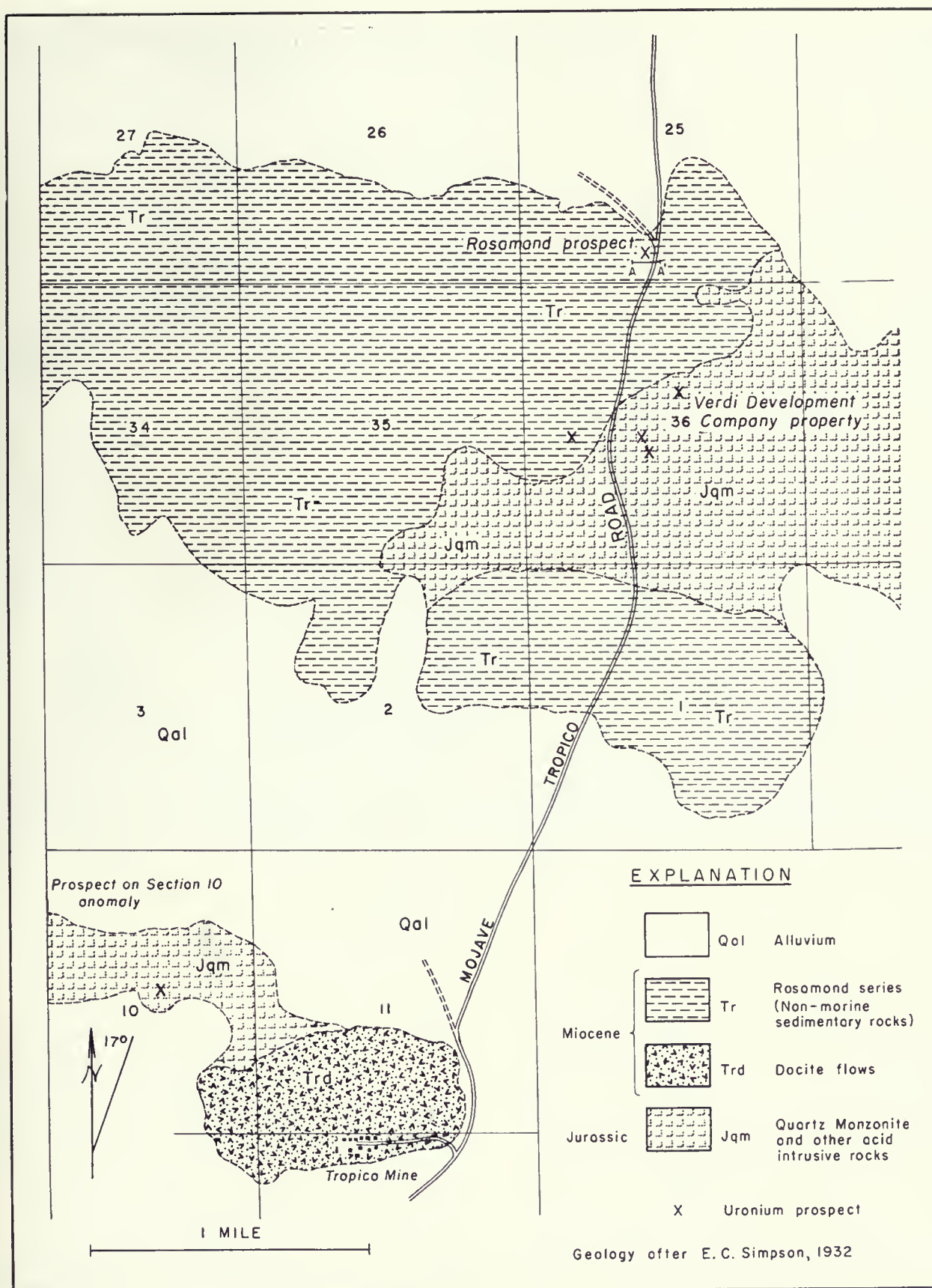


FIGURE 7. Generalized geologic map of Rosamond area, Kern County, showing location of uranium deposits.





FIGURE 8. The "Knoll" working of the Verdi Development Co., near Rosamond, Kern County. Adit extends northwest into volcanic rocks of the Miocene (?) Rosamond series and into quartz monzonite. It follows a north-trending shear zone which contains autunite and uranophane as the principal uranium-bearing minerals.

*Kramer Hills and Harvard Hills, San Bernardino County.* In the Kramer Hills and Harvard Hills in western and central San Bernardino County, carnotite and autunite occur in lake beds of probable Miocene age. The minerals have formed along joints and along bedding surfaces in multi-colored, thin-bedded bentonitic clay beds, silty shale, marly clay beds and opaline shale. The uranium content of even the most radioactive deposits has to date (1956) proved to be sub-commercial, but such deposits constitute a modest reserve of low-grade material that eventually may be worked. In the Kramer Hills, the uranium mineralization is apparently confined to a rather thin succession of the lake beds about 20 or more feet stratigraphically beneath a black andesite flow that commonly caps the low hills in the area. In the Harvard Hills, the uranium minerals are localized in fractures and bedding plane surfaces in nearly flat-lying sedimentary rocks that contain chert and lime-

stone, particularly near the crest of the hills on the north and northwest slopes. Iron oxide stains are common near mineralized areas in both groups of hills.

*Ojai Area, Ventura County.* Secondary uranium minerals have been found in several areas in Ventura County, principally near Ojai. Carnotite and possibly other secondary uranium minerals are associated with pods or lenses of carbonaceous material in sandstone beds that lie within or adjacent to the gradational contact between the Coldwater (Eocene) formation and the Sespe (Oligocene) formation. Other sandstone occurrences are radioactive but contain no exposed carbonaceous material. The extent and grade of these and other similar occurrences are not yet known to the writers, but the gradational contact with which they are associated is extensively exposed in Ventura and Santa Barbara Counties.



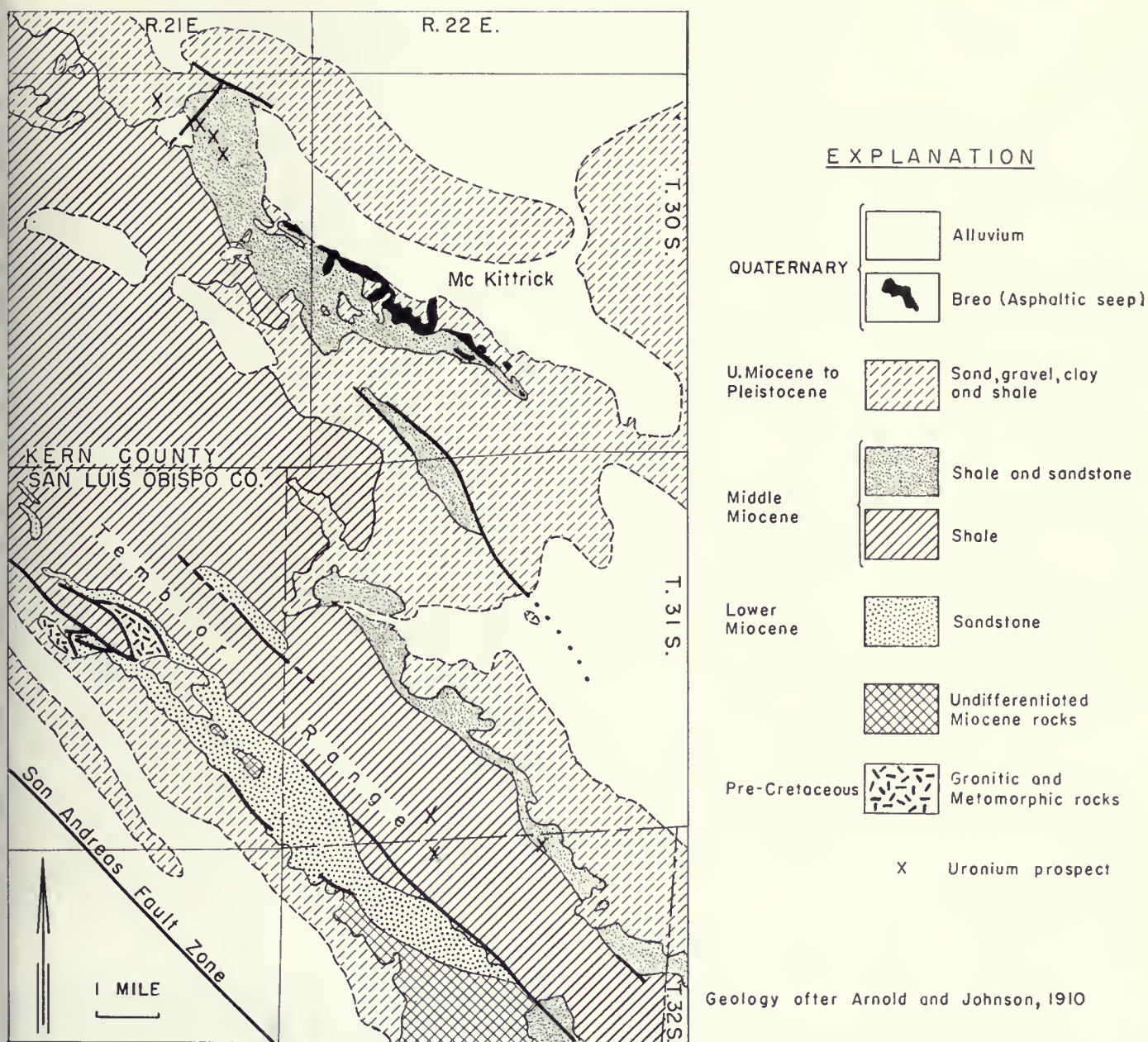


FIGURE 9. Geologic map of part of the Temblor Range, near McKittrick, western Kern County, showing the location of uranium prospects in Miocene sedimentary rocks.

**Rosamond Area, Kern County.** In the Rosamond area, northwest of Rosamond, Kern County (fig. 7), autunite, meta-autunite, uranophane, and gummite (?) occur as coatings on fractures and bedding plane surfaces and as local disseminations adjacent to fault zones. The most common host rocks are tuffaceous sedimentary rocks and volcanic rocks of Miocene (?) age and Mesozoic granitic rocks. Although several properties in this area have been extensively explored, no uranium ore or concentrates had been shipped by mid-1956.

At the property of the Verdi Development Company in the western part of the Rosamond Hills, meta-autunite and uranophane occur as fracture-coatings in granodiorite and tuffaceous sedimentary rocks adjacent to a north-

east-trending fault. The uranium-bearing fractures have been noted as far as 60 feet from the fault and are irregularly distributed along it for at least a mile. A few hundred tons of granodiorite, containing meta-autunite and uranophane, were mined in 1955 and 1956 and processed by leaching in a mill nearby. The ore reportedly contained slightly less than 0.2 percent  $U_3O_8$ , but no concentrates were shipped to the A.E.C.

At the Rosamond prospect (fig. 7), autunite and gummite (?) occur as coatings on fractures and as disseminations in tuffaceous sedimentary rocks adjacent to faults through an area of about 15 acres. Exploration by the Verdi Development Company indicates that the uranium minerals are erratically distributed. The  $U_3O_8$  content



of 12 samples from the area ranged from 0.002 to 0.59 (Walker, 1953, p. 7).

In a nearby property to the southwest, autunite-bearing fractures occur in a porphyritic andesite dike that intrudes quartz monzonite, and in the quartz monzonite as well. The dike is as much as 100 feet thick and is exposed along strike for approximately 2,000 feet. Approximately one carload of uranium-bearing andesite has been stockpiled from a 30-foot deep inclined shaft in the andesite.

*Taft-McKittrick Area, Western Kern County.* Along the eastern flank of the Temblor Range in western Kern County and eastern San Luis Obispo County, secondary uranium minerals occur in upper to middle Miocene marine sedimentary rocks, principally gypsiferous clay shale. The host rocks are locally silicified, and the uranium mineralization has been localized in faults and fractures and bedding planes as well as in a widespread, but very low-grade surface mantle. Since the discovery of uranium near Taft in 1954, at least 36 individual uranium-bearing localities have been reported in this region. A modest amount of exploration work has been done on about 10 of them. Fifty tons of screened fines, collected from shale and containing 0.16 percent  $U_3O_8$ , was shipped from the Owen No. 3 claim, near Taft, in mid-1956. Approximately 30 tons of plus 0.15 percent  $U_3O_8$  uranium-bearing shales has been stockpiled at the Los Amigos claim, also near Taft.

Exploration has extended to a depth of 70 feet in a fault zone at the Surprise No. 1 claim, 5 miles northwest of McKittrick, where meta-autunite occurs as irregular disseminations and thin stringers associated with manganese stains and gypsum. Near the fault zone, the shale host rock contains laminae and cavity fillings of chalcocony.

Most of the deposits along the Temblor Range contain uranium mineralization in bedding planes and in minor fractures. These lie within 10 to 20 feet of the surface, and contain 0.10 percent  $U_3O_8$  or less. Individual bodies of this type may be as much as an acre in areal extent. Within these low-grade surface deposits, faults and fracture zones may have a higher uranium content which may extend to depths greater than 20 feet.

*Southern Sierra Nevada, Kern County.* Most of the uranium occurrences that have been found to date in the southern Sierra Nevada are in rocks of Mesozoic age or older. Two, however, are uraniferous bog deposits of Recent age. Secondary uranium minerals, principally autunite and carnotite, have been localized in fractures in granitic and metamorphic rocks, but in a few places primary minerals have been found. The properties include the Miracle and Kergon mines along the Kern River, near Miracle Hot Springs; the Embree property along Erskine Creek and about 8 miles east of Miracle Hot Springs; and the Kervin and Lucky Seven claims about 10 miles east of the Embree property, in Kelso Valley. One uraniferous bog deposit is near the Miracle mine; the other is about 100 miles north in Fresno County.

In the vicinity of the Miracle mine and Kergon mine (figs. 10, 11) autunite and other uranium-bearing minerals occur in clayey gouge and altered zones in sheared Mesozoic quartz diorite. Autunite is the principal ore

mineral, but, in addition, carnotite (tyuyamunite ?) is common, and uranophane, walpurgite, and sooty pitchblende (Wood 1956, p. 537) have been identified. The associate minerals include abundant limonite, subordinate roscoelite (vanadium-bearing mica) and minor fluorite and ilsemannite (hydrous molybdenum oxide).

The principal ore control at the Miracle mine is a northwest-trending, vertical shear zone. It has been developed by a 255-foot drift adit and numerous surface cuts. Uranium mineralization at the nearby Kergon mine has been controlled by a prominent fault which trends northeast and dips steeply to the west. A north-trending, altered and shattered zone which diverges from the hanging wall of the main fault also is mineralized. It has been developed by a 65-foot inclined shaft.

Four carloads of uranium ore have been shipped from these mines. On July 31, 1954, forty-six tons that averaged 0.62 percent  $U_3O_8$  was shipped from the Miracle mine. A second carload of ore was shipped in July 1955. Two carloads of ore from the Kergon mine were shipped in 1955. One averaged 0.16 percent  $U_3O_8$ , the other averaged 0.22 percent  $U_3O_8$ .

Primary uranium minerals, tentatively identified as pitchblende and gummite, and very subordinate yellow secondary uranium minerals have been found at the Embree property (fig. 11). The mineralization occurs in quartzite and appears to be associated with dark gray to black streaks which lie near and roughly parallel to a contact with gneiss. This contact has been explored by two underground workings, one about 165 feet in total length, the other about 205 feet long. By 1956, no ore shipments had been made. Samples collected from the property assayed as much as 3 percent  $U_3O_8$  (Walker, Lovering, and Stephens, 1956, p. 30). At the Kervin and Lucky Seven prospects in Kelso Valley (fig. 11), secondary uranium minerals are localized in sheared and altered granodiorite adjacent to contacts with pre-Cretaceous metasedimentary rocks. Autunite, meta-autunite, torbernite, and uranocircite have been found to a depth of 25 feet in exploration cuts and shafts. No ore has been shipped to date (1956).



FIGURE 10. View southwest toward ore chute of the Miracle mine, along State Highway 178, Kern County. Northwest-trending shear zone which contains the secondary uranium minerals is nearly directly beneath the ore chute and underlies the topographic depression which extends toward upper left of photo. Initial discovery from car was in roadcut near the truck.



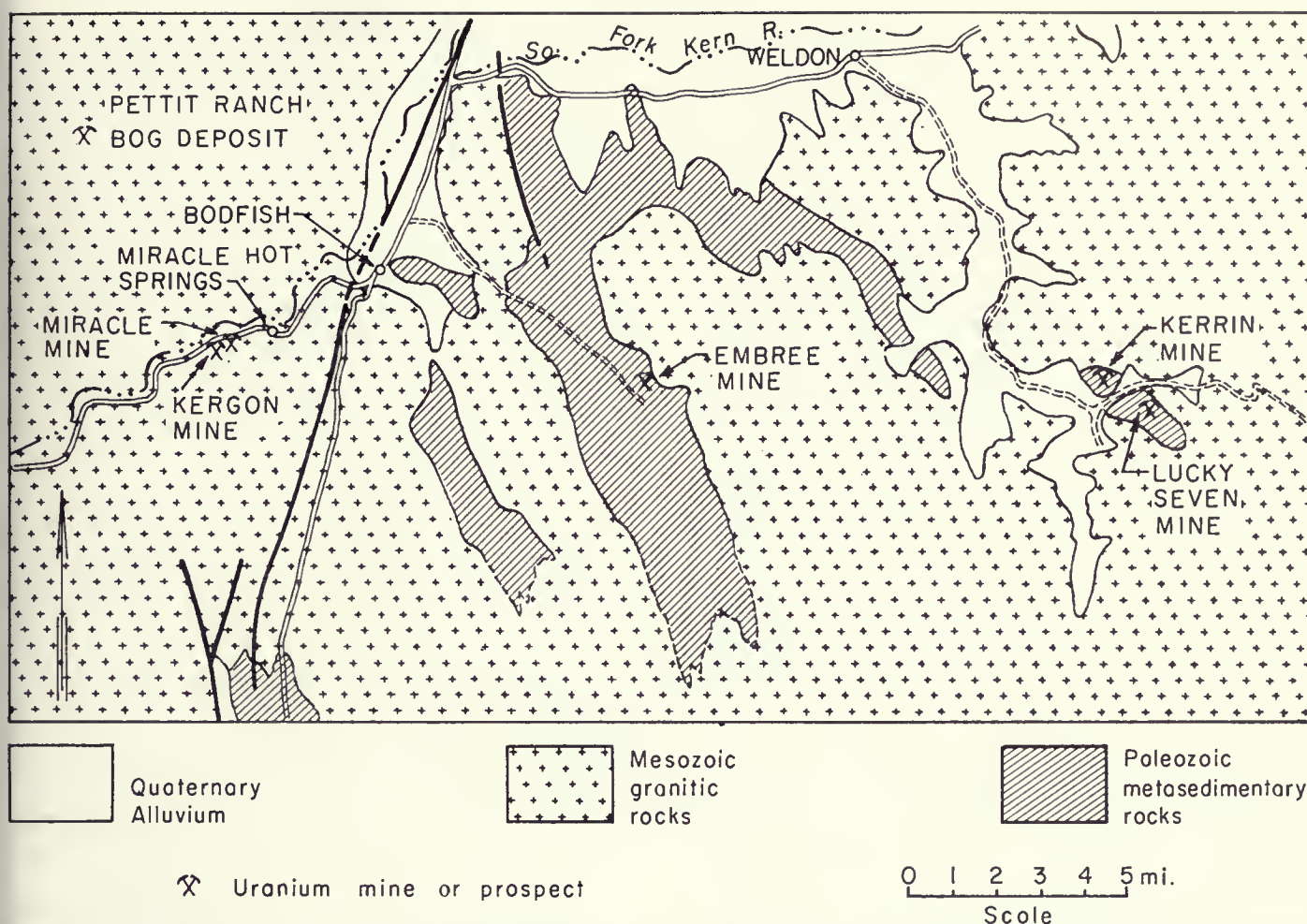


FIGURE 11. Generalized geologic map of part of the southern Sierra Nevada, Kern County, showing the location of some of the uranium deposits. Geology from *Geologic Map of California*, scale 1:250,000, Bakersfield sheet, 1955.

The uraniferous bog on Pettit Ranch, 6 miles northwest of the Miracle mine, is about 1,000 feet long, 100 to 300 feet wide, and 2 to 10 feet thick. It is composed of woody fragments, black carbonaceous matter, silt, and arkosic sands, and in general, grades downward into decomposed granodiorite. The bog overlies an east-northeast-trending fault zone and is perched above the channel of Little Poso Creek, into which it drains. Water flowing into the bog contains an appreciable amount of uranium and is believed to have risen along the fault. As the water percolates through the bog, the uranium is adsorbed by the peat. Although no uranium minerals have been identified, the average  $U_3O_8$  content of the peat is about 0.10 percent. Analyses by the U. S. Bureau of Mines show that water entering the peat bog has a higher uranium content than that draining from it, and indicate that uranium is now being deposited.

At Hoffman Meadow, in Fresno County, and nearly 100 miles north of Pettit Ranch, two bogs are perched above Hoffman Creek, a tributary of San Joaquin River, and occupy topographic depressions above a north-northeast-trending fault zone. One bog is 200 feet wide by 400 feet long, the other is 200 feet wide by 500 feet long.

They are from 2 to 6 feet thick. The geologic and mineralogic features of the Hoffman Meadow bogs are similar to those on Pettit Ranch, but sampling indicates that the  $U_3O_8$  content of the peat at Hoffman Meadow is about 0.24 percent.

*Prospecting in California.* The uranium prospector in California, as elsewhere, should have a general knowledge of the mode of occurrence of uranium and the minerals with which it is associated. Excellent summaries of this subject are presented in various books, some of which are listed in the references at the end of this section. As most discoveries of uranium deposits have been made in areas of known uranium mineralization, prospectors should consider such areas as those described above carefully. Examination of old mine dumps affords a rapid and economical method of checking materials recovered from mines, many of which are now inaccessible to prospecting.

H. G. Stephens (personal communication, 1955) has emphasized the fact that most of the radioactive deposits in California have been found in areas that receive less than 20 inches of precipitation annually (fig. 1). This suggests that near-surface concentrations of water-sol-



uble secondary uranium minerals are more apt to be found in arid regions where water does not carry the uranium away in solution. Moreover, such removal of secondary minerals, which are commonly guides to deposits of primary minerals, causes the primary minerals to be more difficult to find.

#### DEVELOPMENT OF MINES AND MARKETING OF URANIUM ORES \*

The U. S. Atomic Energy Commission controls the transfer and sale of uranium and thorium source materials in the United States and also purchases domestic ores or concentrates of such material. Other concerns can purchase such materials only with special permission of the Commission. Table 1 contains a summary of the history of the control of radioactive source materials in the United States. As the Commission is committed to buy only certain types of uranium ore (i.e., carnotite- and roscoelite-types common to deposits on the Colorado Plateau), the sale of such ores as have been found in California must be negotiated.

Upon discovery of a radioactive locality, the prospector should determine whether the radioactive material is uranium, thorium, or any other radioactive substance, and if it is of commercial grade. If possible, representative samples of the radioactive rock should be submitted to a commercial assayer or to certain offices of the Atomic Energy Commission or U. S. Bureau of Mines, or both. For government assays, representative samples of at least 1 pound should be sent either to the Reno office of the U. S. Bureau of Mines or to the nearest field office of the Atomic Energy Commission, to be forwarded to their laboratory. Field offices have been established in Bakersfield, California, Las Vegas, Nevada, and Reno, Nevada. A radiometric assay will be made and, if warranted, a chemical assay, as well. If the sample proves of interest, the Commission will be advised and a form requesting further information will be sent to the person who submitted the sample. Should the property appear to warrant a field examination, this will be scheduled by a representative from the appropriate field office. The field representative will examine the property, make preliminary maps, and collect samples if advisable.

During early development of a property, most exploration work is limited to surface study and sampling. Many claim owners seek the assistance of qualified consulting mining engineers and geologists in the preparation of geologic maps and in the establishment of an exploration program which generally consists of trenching, drilling, shallow subsurface exploration, or combinations of the three. Properties that appear to contain mineable ore bodies can then be more seriously developed.

Most exploration programs are expensive and may require outside financing. This can be obtained by raising private capital through partnerships, by incorporating and selling stock, or by securing an exploration loan from the United States Government. Loans for exploration are administered by the Defense Minerals Explorations Administration of the U. S. Department of the

Interior. For uranium exploration, the agency will furnish 75 percent of the capital necessary to develop a prospect that it considers to be favorable. Repayment of approved loans is made to the Government by royalty on production from the property. Loans for actual mining or milling are available from the Small Business Administration of the United States Government.

Uranium ores can be sold only to the Atomic Energy Commission or to agents of their selection. The Commission not only buys the ore at a guaranteed price, but pays an initial production bonus on the first 10,000 pounds of  $U_3O_8$  from a qualified property. The Commission also includes partial payment for mine development and haulage, and makes additional payments for higher grade ores. Table 2 shows the Commission's price schedule which is effective until March 31, 1962. After that date, only mill concentrates will be purchased by the Commission (see table 1).

The Commission will also pay a bonus of \$10,000 for the discovery and delivery of the first 20 short tons of non-carnotite uranium ores or mechanical concentrates, assaying 20 percent or more  $U_3O_8$ , from a single mining location which has not previously been worked for uranium.

Before any shipments of ore can be made to the Commission, a license must be procured and a contract negotiated. Application for licenses are made to the Licensing Controls Branch, Washington, D. C. on form AEC-2 which can be obtained from any office of the Commission. Contracts for delivery of ore are negotiated with the Mining Division of the Commission in Grand Junction, Colorado.

The initial production bonus is payable after a shipment of ore has been made and paid for. Application for certification of the mining property for bonus payments should be completed on form AEC-299 and forwarded to the Mining Division, Grand Junction Operations Office. After certification, bonuses will be paid monthly on shipments upon request of the shipper. Contracts for the sale of ore to the Commission are negotiated with the Mining Division of the Grand Junction Operations Office. The Commission determines which mill will receive the ore, depending on the type. Most of the ore from California has been shipped in 45-ton carload lots to Salt Lake City, Utah. Ordinarily ore that contains less than 0.2 percent  $U_3O_8$  (4 pounds per ton) cannot be economically shipped from California. The prices paid for the ore at the mill or buying station include the grade premium, mine development allowance, and haulage allowance. A haulage allowance of 6 cents per ton-mile is payable up to 100 miles maximum from mine to delivery point (a maximum of \$6.00 per ton for acceptable ores).

The Commission does not restrict or regulate the construction or location of a uranium mill, but it will not buy the mill products except by contract. Permits and contracts for selling concentrates are negotiated through the Concentrate Procurement Division of the Grand Junction Operations office.

\* Much of this information was kindly furnished by E. E. Thurlow and A. E. Granger, U. S. Atomic Energy Commission.



Table 1. Chronological summary of United States regulations governing prices, ownership, and disposal of domestic and foreign radioactive and fissionable substances.

Date			Title of regulation or release	Summary of applicable parts of regulation
Enacted	Effective	Expiration		
26 Jan 43	26 Jan 43		Conservation Order N-285 U. S. War Production Board.	Uranium metal, uranium salts and other uranium compounds, and any alloy or mixture containing 1/10 of 1 percent (0.10) or more uranium by weight, including crude ores and residues and matte, cannot be sold, delivered, purchased, or received for use in the manufacture or decoration of glass, glassware, pottery, tile, or other ceramic products.
13 Sep 45	13 Sep 45	4 Mar 46	Executive Order 9613 by President of the U. S.	Withdraws from sale or other forms of disposal (including mineral locations) all applicable U. S. public lands that contain deposits of radioactive substances and all deposits of such substances. Such lands are reserved from sale by U. S. and U. S. retains right to enter upon such lands and mine and remove such minerals.
4 Mar 46	4 Mar 46	5 Dec 47	Executive Order 9701 by President of the U. S.	Revokes Executive Order 9613. Provides that all public lands of the U. S. which contain or may contain fissionable materials shall be subject to disposal under public lands laws or lease, permit, or other authorization to use the land provided reservation is made that U. S. can enter upon land and prospect for, mine, and remove fissionable materials. Fissionable materials are defined as all deposits from which the substances known as thorium, uranium, and elements higher than uranium in the periodic table, can be refined or produced and all deposits from which there can be refined or produced other substances readily capable of or peculiar to transmutation of atomic species, the production of nuclear fission, or the release of atomic energy.
1 Aug 46	1 Aug 46		Atomic Energy Act of 1946 (Public Law 585-79th Congress).	Establishes Atomic Energy Commission. Unlawful for any person to possess, transfer, export from or import into U. S., or produce fissionable material. Must have license to transfer, deliver, receive, or export from U. S. quantities of source material in excess of amounts deemed important by the Commission. The Commission may purchase, take, requisition, or otherwise acquire source materials. The Commission may establish guaranteed prices. Public lands containing source material reserved for U. S.
31 Dec 46	1 Jan 47		Executive Order 9816 by President of the U. S.	Manhattan District control transferred to the Atomic Energy Commission.
17 Mar 47	1 Apr 47		Source Material Control, Atomic Energy Commission.	Source material defined as any material, except fissionable material, which contains by weight 0.05 percent or more of uranium, thorium, or any combination thereof. No person, unless licensed by the Commission may transfer, deliver, receive possession of or title to, or export from the U. S. any source material after removal from its place of deposit in nature except a person may move in any calendar month a quantity of raw source material that contains less than 10 pounds of uranium, thorium, or any combination thereof. These regulations not applicable for certain manufactured products. Certain uses for uranium are prohibited.
5 Dec 47	5 Dec 47		Executive Order 9908 by President of the U. S.	Revokes Executive order 9701. Provides for reservation of source material in certain lands owned by the U. S. not regulated by Atomic Energy Act of 1946.
9 Apr 48	12 Apr 48	12 Apr 58	Circular 1, Atomic Energy Commission.	Ten year guaranteed price for domestic uranium ores exclusive of carnotite-type or roscoelite-type ores of the Colorado Plateau. Establishes a guaranteed minimum price for domestic uranium-bearing ores and mechanical concentrates of \$3.50 per pound of $U_3O_8$ recoverable, less cost per pound of refining. Guarantees price of \$3.50 per pound of contained $U_3O_8$ refined. Prices on the basis of dry weight f.o.b. shipping point designated by the Commission. Establishes minimum quantity and grade acceptable as 10 tons (20,000 pounds) containing at least 10 percent $U_3O_8$ (either as ores or mechanical concentrates) or 1 ton (2,000 pounds) of refined uranium of at least 97 percent $U_3O_8$ in black uranium oxide or 87 percent $U_3O_8$ in sodium uranate. Negotiations can be made for lesser amounts and for larger quantities at higher prices for which refining and milling costs, transportation costs, and other factors are taken into consideration. Consideration is given for other recoverable valuable constituents in ore.
9 Apr 48	12 Apr 48		Circular 2, Atomic Energy Commission.	Bonus program for discovery and delivery of new highgrade domestic uranium deposits. A bonus, in addition to prices paid according to Circular 1, of \$10,000 is paid for the delivery of the first 20 short tons or uranium-bearing ores or mechanical concentrates assaying 20 percent or more $U_3O_8$ from any single mining location which has not previously been worked for uranium. Not applicable to carnotite-type or roscoelite-type ores of the Colorado Plateau.
9 Apr 48	12 Apr 48	12 Apr 51	Circular 3, Atomic Energy Commission.	Three year guaranteed minimum price for uranium-bearing carnotite-type or roscoelite-type ores of the Colorado Plateau area. Deliveries not in excess of 1,000 tons per calendar year can be made without a contract. Deliveries in excess of 1000 tons per year can be made after contract has been made but can be limited to 5000 tons per calendar year. Deliveries must be made to buyer's depot established by the Commission and must not be made in less than 10-ton lots. Schedule of prices: 30c per pound to \$1.50 per pound of $U_3O_8$ for ores assaying .10 percent to .15 percent and \$1.50 per pound for $U_3O_8$ in ores assaying more than .15 percent. A development allowance of 50c per pound of $U_3O_8$ is paid for ores that assay .15 percent $U_3O_8$ or more. A premium of 25c per pound of $U_3O_8$ is paid for each pound in excess of 4 pounds per ton and 25c additional for each pound of $U_3O_8$ in excess of 10 pounds per ton. Payment schedule for vanadium, limit on lime content.
15 Jun 48	1 Jun 48	1 Jul 49	Circular 4, Atomic Energy Commission.	Temporary additional allowance for ores covered by Circular 3. Authorizes a haulage allowance of 6c per ton mile for acceptable ores from mine to mill up to a maximum of 100 miles. Payment of 50c per pound of $U_3O_8$ in excess of 4 pounds per ton (0.2 percent). (See other circulars below).



*Table 1. Chronological summary of United States regulations governing prices, ownership, and disposal of domestic and foreign radioactive and fissionable substances—Continued*

Date			Title of regulation or release	Summary of applicable parts of regulation
Enacted	Effective	Expiration		
7 Feb 49	1 Mar 51	30 Jun 54	Circular 5, Atomic Energy Commission.	Increase of guaranteed minimum prices and extension of time for purchase program for carnotite-type or roscoelite-type ores of the Colorado Plateau area. Schedule of prices: 50¢ per pound to \$2.00 per pound of U <sub>3</sub> O <sub>8</sub> for ores assaying .10 percent to .20 percent and \$2.00 per pound for U <sub>3</sub> O <sub>8</sub> in ores assaying more than .20 percent. A development allowance of 50¢ per pound of U <sub>3</sub> O <sub>8</sub> is paid for each pound in excess of 4 pounds per ton and 25¢ additional for each pound of U <sub>3</sub> O <sub>8</sub> in excess of 10 pounds per ton. Payment schedule for vanadium, limit on lime content. Haulage allowance of 6¢ per ton mile for acceptable ores from mine to mill up to a maximum of 100 miles.
20 Oct 50		31 Mar 58	Circular 5	Extension of time for Circular 5.
26 Feb 51	1 Mar 51	31 Mar 58	Circular 5, revised.	Increase of guaranteed minimum prices for purchase of carnotite-type or roscoelite-type ores of the Colorado Plateau area. Schedule of prices: \$1.50 per pound to \$3.50 per pound of U <sub>3</sub> O <sub>8</sub> for ores assaying .10 percent to .20 percent and \$3.50 per pound for U <sub>3</sub> O <sub>8</sub> in ores assaying more than .20 percent. A development allowance of 50¢ per pound of U <sub>3</sub> O <sub>8</sub> is paid for each pound in acceptable ores. A grade premium of 75¢ per pound is paid for each pound of U <sub>3</sub> O <sub>8</sub> in excess of 4 pounds per ton plus 25¢ additional for each pound in excess of 10 pounds of U <sub>3</sub> O <sub>8</sub> per ton. A haulage allowance of 6¢ per ton mile is paid on acceptable ore up to a maximum of 100 miles. Payment of 31¢ per pound up to, but not exceeding, 10 pounds of V <sub>2</sub> O <sub>5</sub> for each pound of U <sub>3</sub> O <sub>8</sub> . Minimum ore grade accepted is .10 percent U <sub>3</sub> O <sub>8</sub> . Maximum allowable lime is 6 percent.
27 Jun 51	1 Mar 51	28 Feb 57	Circular 6, Atomic Energy Commission.	Establishes bonus for initial production of uranium ores from eligible new domestic mines. Authorizes payment of bonus for first 10,000 pounds of U <sub>3</sub> O <sub>8</sub> from new mines as follows: \$1.50 per pound to \$3.50 per pound of U <sub>3</sub> O <sub>8</sub> for ores assaying .10 percent to .20 percent and \$3.50 per pound for U <sub>3</sub> O <sub>8</sub> in ores assaying more than .20 percent. (See A.E.C. release No. 830 below).
9 Oct 53		31 Mar 62 28 Feb 57	Circular 5, Revised Circular 6.	Extension of time for Circular 5, revised and Circular 6.
29 Jan 54	29 Jan 54	12 Dec 54	Circular 7, Atomic Energy Commission.	Regulates leasing of certain public lands for uranium mining purposes.
13 Aug 54	12 Dec 54		Public Law 585, 83rd Congress.	Permits multiple use of public lands. Revokes reservation of uranium on public lands to the U. S.
30 Aug 54	30 Aug 54		Atomic Energy Act of 1954 (Public Law 703-83rd Congress-2nd Session).	"Modernization" of Atomic Energy Act of 1946. No basic changes in control. Adds to definition of source material—ores—in such concentration as the Commission may by regulation determine from time to time.
18 Mar 56	1 Apr 56			Two schedules of prices established for uranium ores that contain more than 6 percent lime (for ore buying stations at Moab and Monticello, Utah, only). Schedule I: Same as circular 5, revised except that a deduction will be made of \$1.00 plus 30¢ per dry ton for each percent of lime in excess of 6 percent or—Schedule II: Same as circular 5, revised except that no payment will be made for vanadium or any other constituent of the ore.
24 May 56	24 May 56	See Summary	Release No. 830, Atomic Energy Commission.	Extends time limit of initial production bonus from 28 Feb. 1957 to 31 Mar. 1960 (See Circular 6, above). Establishes new uranium procurement for domestic uranium concentrates, rather than ores, from 1 April 62 through 31 Dec. 66 (after Circular 5, revised expires). Base price of \$8.00 per pound of U <sub>3</sub> O <sub>8</sub> contained in concentrates. Commission has option to limit purchases of concentrates from any single mining property to 500 tons of U <sub>3</sub> O <sub>8</sub> in any calendar year, except that additional concentrates may be purchased at lower prices. No commitment to buy vanadium. Producers will be able to sell to licensed commercial users.

Listed below are addresses of the U. S. Government agencies that offer assistance to uranium prospectors:

For sample analyses:

Rare and Precious Metals Experiment Station  
U. S. Bureau of Mines  
1605 Evans Avenue  
Reno, Nevada

Field offices of Salt Lake area office:

U. S. Atomic Energy Commission  
Bakersfield Field Office  
Haberfelde Building  
Room 558, 1706 Chester Avenue  
Bakersfield, California

U. S. Atomic Energy Commission  
Division of Raw Materials  
P. O. Box 2088  
Las Vegas, Nevada

U. S. Atomic Energy Commission  
Division of Raw Materials  
U. S. Bureau of Mines Building  
Room 304, 1605 Evans Avenue  
Reno, Nevada

Licenses:

Licensing Controls Branch  
Division of Construction and Supply  
U. S. Atomic Energy Commission  
1901 Constitution Avenue  
Washington 25, D. C.



**Contracts for ore:**

U. S. Atomic Energy Commission  
Grand Junction Operations Office  
Grand Junction, Colorado  
Attention: Mining Division

**Contracts for concentrates (mill product):**

U. S. Atomic Energy Commission  
Grand Junction Operations Office  
Grand Junction, Colorado  
Attention: Concentrate Procurement Div.

**Loans for mineral explorations:**

Defense Minerals Exploration Administration  
U. S. Bureau of Mines Building  
1605 Evans Avenue  
Reno, Nevada

**Loans for mining:**

Small Business Administration  
1031 South Broadway  
Los Angeles 15, California

Small Business Administration  
Flood Building  
870 Market Street  
San Francisco 2, California

**General Information:**

U. S. Atomic Energy Commission  
Division of Raw Materials  
Salt Lake Area Office  
P. O. Box 2196  
Salt Lake City, Utah

**TESTING FOR URANIUM**

All radioactive elements emit alpha or beta particles, and some emit gamma rays or a combination of beta particles and gamma rays. Alpha particles (or "alpha-rays") are heavy enough to produce high ionization in the air through which they travel, but their range in air is so short that they are not useful in detecting uranium with ordinary instruments. Beta particles (or "beta-rays") are electrons which can travel several yards in air, but whose range in solid material is short. They can be detected with geiger counters, but are not as useful as gamma rays as indicators. Gamma rays are true radiation of the same type as ordinary light, x-rays, and radio waves. Although they have much higher energy than the other types of radiation, as well as much shorter wave lengths, and a higher penetrating power, they are absorbed by approximately 1 foot of rock.

Radioactivity may be detected in a number of ways, but the most practical portable prospecting instruments are geiger counters and scintillation counters. A great quantity of information regarding the use of these instruments is readily available in many publications. As radiation affects photographic plates or films in much the same way as light, these materials afford a relatively simple method of detecting the presence of uranium- or thorium-bearing minerals in rocks and also a method of locating radioactive mineral grains in a specimen. The specimen should be ground flat on one side and smoothed with fine emery, cleaned and dried, and the ground surface placed directly on the emulsion coated side of a photographic plate or film and held in position by adhesive tape. An outline of the flat surface should be drawn with a pencil to show the position of the specimen when the film is developed. An exposure time of a week or longer is usually necessary.

When alpha particles from radioactive substances strike a screen coated with activated zinc sulfide, they produce tiny flashes of light, which can be readily seen in the dark with a low-power microscope. A spintharoscope or "scintilloscope" is a small instrument consisting of a zinc sulfide screen and focusing tube magnifier. The instrument can only be used in the dark after the observer's eyes have become accustomed to darkness. Also, it is necessary to wait for some time for flashes from low-grade material. The advantages of this instrument are its low cost, small size, high efficiency, and ease with which the source of the alpha particles observed can be isolated.

Simple chemical tests can be performed to determine whether uranium or thorium is present in a radioactive specimen. These usually involve at least a partial mineral identification. A confirmation of the presence of uranium can be obtained with a simple fluorescent bead test with sodium fluoride. Nonfluorescent or weakly fluorescent beads are obtained from most thorium-bearing minerals.

**PROCESSING OF ORES**

As uranium ores range widely in their chemical and physical properties, they are processed in numerous ways. The U. S. Atomic Energy Commission has classified uranium ores into 28 metallurgical types based on the solubility of the uranium minerals, lime (calcium carbonate) content, kind of host rock or gangue, presence of sulfides, and carbon content. The processing of uranium ore is a complex procedure to which new techniques are being continually added. Mills constructed in the western U. S. have cost about \$10,000 per ton of daily capacity (Mitchell, 1956). Advances in metallurgical technology, however, have reduced costs of treatment per ton so that low-grade ores containing as little as 0.1 percent  $U_3O_8$  are blended into mill feed.

All of the uranium mills that treat ores from the western U. S. employ chemical processes. Nearly all of these ores are processed by acid leaching or carbonate leaching, depending primarily on the lime content of the ore. The uranium ores produced to date in California have been low in lime, and have been processed by acid leaching in the mill of Vitro Uranium Company, Salt Lake City, Utah.

The principal steps in the concentration of uranium ore are (1) ore preparation (grinding, physical concentration, and blending), (2) ore pretreatment (roasting, acid cure, etc.), (3) leaching, (4) liquid-solid separation, (5) uranium recovery, and (6) uranium refining. The refined concentrates (high-purity uranium compounds) are sold to the Atomic Energy Commission and are subsequently converted to "orange oxide," the pure uranium trioxide, which is the basic uranium chemical used for production of other uranium salts, metal, and enriched uranium.

Before August 1955, much of the information concerning processing of domestic uranium ores was classified, but since that time the Atomic Energy Commission has permitted the release of such information. Two excellent summaries (Irani, 1956, Lennemann, 1956) were the principal sources of information for the following discussion.



Table 2. Schedule of prices for uranium ore as specified in Circular 5, Revised and Circular 6, U. S. Atomic Energy Commission (see also table 1).

Grade of ore, percent U <sub>3</sub> O <sub>8</sub>	Pounds of U <sub>3</sub> O <sub>8</sub> per ton of ore	Base price		Grade premium		Mine develop. allowance .50/lb.	Price per ton of ore		
		Pound U <sub>3</sub> O <sub>8</sub>	Ton of ore	75¢ a lb. over 4-lb.	25¢ a lb. over 10-lb.		Price before initial prod. bonus and haul- age allowance	Initial prod. bonus on 10,000 lbs.	Price before haulage allowance
0.10.....	2.00	\$1.50	\$3.00	--	--	\$1.00	\$4.00	\$3.00	\$7.00
0.11.....	2.20	1.70	3.74	--	--	1.10	4.84	3.74	8.58
0.12.....	2.40	1.90	4.56	--	--	1.20	5.76	4.56	10.32
0.13.....	2.60	2.10	5.46	--	--	1.30	6.76	5.46	12.22
0.14.....	2.80	2.30	6.44	--	--	1.40	7.84	6.44	14.28
0.15.....	3.00	2.50	7.50	--	--	1.50	9.00	7.50	16.50
0.16.....	3.20	2.70	8.64	--	--	1.60	10.24	8.64	18.88
0.17.....	3.40	2.90	9.86	--	--	1.70	11.56	9.86	21.42
0.18.....	3.60	3.10	11.16	--	--	1.80	12.96	11.16	24.12
0.19.....	3.80	3.30	12.54	--	--	1.90	14.44	12.54	26.98
0.20.....	4.00	3.50	14.00	--	--	2.00	16.00	14.00	30.00
0.21.....	4.20	"	14.70	\$0.15	--	2.10	16.95	14.70	31.65
0.22.....	4.40	"	15.40	0.30	--	2.20	17.90	15.40	33.30
0.23.....	4.60	"	16.10	0.45	--	2.30	18.85	16.10	34.95
0.24.....	4.80	"	16.80	0.60	--	2.40	19.80	16.80	36.60
0.25.....	5.00	3.50	17.50	0.75	--	2.50	20.75	17.50	38.25
0.26.....	5.20	"	18.20	0.90	--	2.60	21.70	18.20	39.90
0.27.....	5.40	"	18.90	1.05	--	2.70	22.65	18.90	41.55
0.28.....	5.60	"	19.60	1.20	--	2.80	23.60	19.60	43.20
0.29.....	5.80	"	20.30	1.35	--	2.90	24.55	20.30	44.85
0.30.....	6.00	3.50	21.00	1.50	--	3.00	25.50	21.00	46.50
0.31.....	6.20	"	21.70	1.65	--	3.10	26.45	21.70	48.15
0.32.....	6.40	"	22.40	1.80	--	3.20	27.40	22.40	49.80
0.33.....	6.60	"	23.10	1.95	--	3.30	28.35	23.10	51.45
0.34.....	6.80	"	23.80	2.10	--	3.40	29.30	23.80	53.10
0.35.....	7.00	3.50	24.50	2.25	--	3.50	30.25	24.50	54.75
0.36.....	7.20	"	25.20	2.40	--	3.60	31.20	25.20	56.40
0.37.....	7.40	"	25.90	2.55	--	3.70	32.15	25.90	58.05
0.38.....	7.60	"	26.60	2.70	--	3.80	33.10	26.60	59.70
0.39.....	7.80	"	27.30	2.85	--	3.90	34.05	27.30	61.35
0.40.....	8.00	3.50	28.00	3.00	--	4.00	35.00	28.00	63.00
0.41.....	8.20	"	28.70	3.15	--	4.10	35.95	28.70	64.65
0.42.....	8.40	"	29.40	3.30	--	4.20	36.90	29.40	66.30
0.43.....	8.60	"	30.10	3.45	--	4.30	37.85	30.10	67.95
0.44.....	8.80	"	30.80	3.60	--	4.40	38.80	30.80	69.60
0.45.....	9.00	3.50	31.50	3.75	--	4.50	39.75	31.50	71.25
0.46.....	9.20	"	32.20	3.90	--	4.60	40.70	32.20	72.90
0.47.....	9.40	"	32.90	4.05	--	4.70	41.65	32.90	74.55
0.48.....	9.60	"	33.60	4.20	--	4.80	42.60	33.60	76.20
0.49.....	9.80	"	34.30	4.35	--	4.90	43.55	34.30	77.85
0.50.....	10.00	3.50	35.00	4.50	--	5.00	44.50	35.00	79.50
0.60.....	12.00	"	42.00	6.00	\$0.50	6.00	54.50	42.00	96.50
0.70.....	14.00	"	49.00	7.50	1.00	7.00	64.50	49.00	113.50
0.80.....	16.00	"	56.00	9.00	1.50	8.00	74.50	56.00	130.50
0.90.....	18.00	"	63.00	10.50	2.00	9.00	84.50	63.00	147.50
1.00.....	20.00	3.50	70.00	12.00	2.50	10.00	94.50	70.00	164.50
2.00.....	40.00	"	140.00	27.00	7.50	20.00	194.50	140.00	334.50
3.00.....	60.00	"	210.00	42.00	12.50	30.00	294.50	210.00	504.50
4.00.....	80.00	"	280.00	57.00	17.50	40.00	394.50	280.00	674.50
5.00.....	100.00	"	350.00	72.00	22.50	50.00	494.50	350.00	844.50
6.00.....	120.00	3.50	420.00	87.00	27.50	60.00	594.50	420.00	1,014.50
7.00.....	140.00	"	490.00	102.00	32.50	70.00	694.50	490.00	1,184.50
8.00.....	160.00	"	560.00	117.00	37.50	80.00	794.50	560.00	1,354.50
9.00.....	180.00	"	630.00	132.00	42.50	90.00	894.50	630.00	1,524.50
10.00.....	200.00	"	700.00	147.00	47.50	100.00	994.50	700.00	1,694.50

**Ore Preparation.** Uranium ores are reduced in size by standard methods of crushing and grinding and are commonly blended to afford a uniform mill feed. Most uranium minerals are not high enough in specific gravity, are too soft, and are too finely disseminated to be upgraded by mechanical or flotation methods as they would be lost in the slimes.

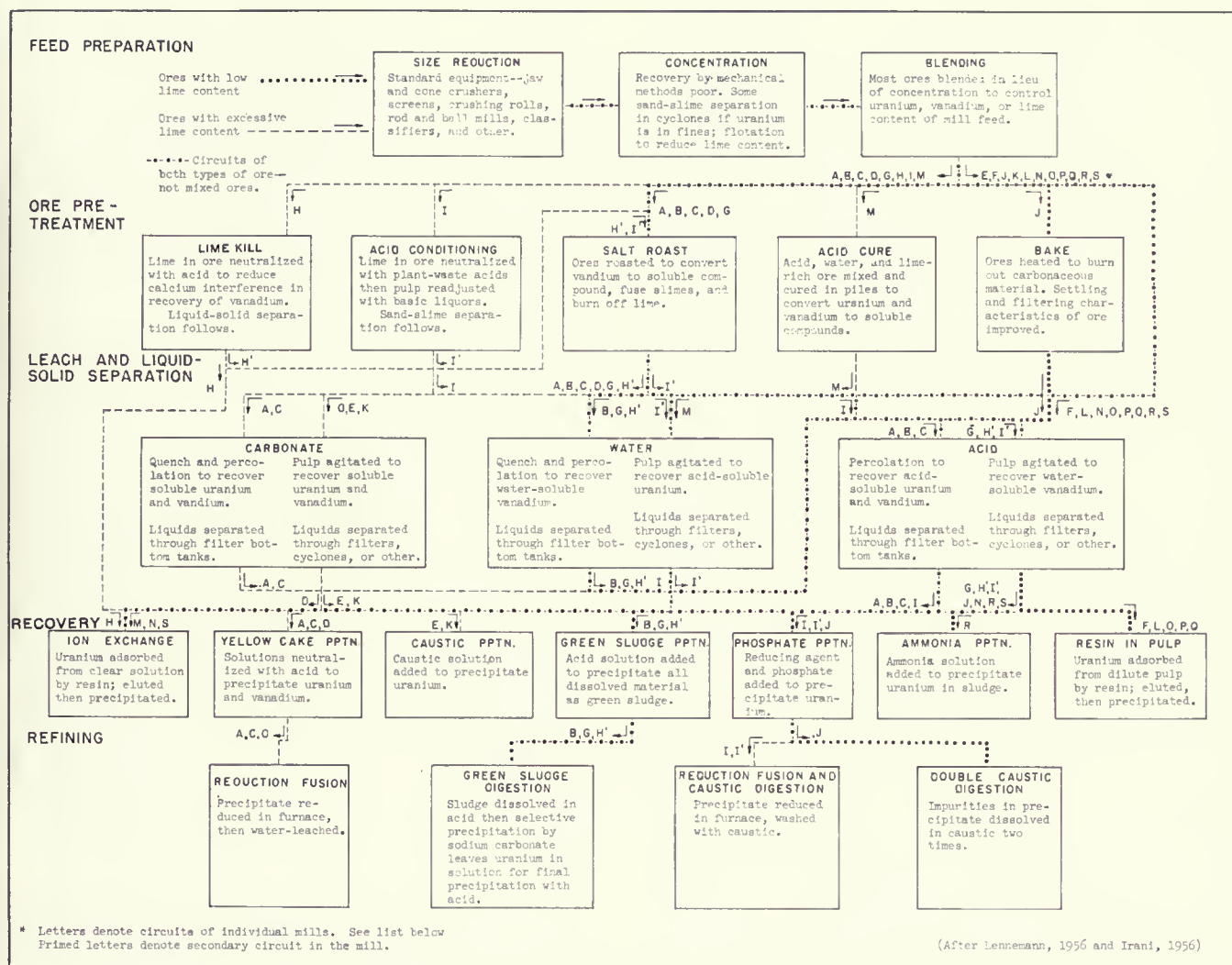
**Ore Pretreatment.** Pretreatment is employed to convert uranium and vanadium to soluble compounds, reduce slime content, lower the lime content, and increase settling and filtering characteristics of ores. The principal types of pretreatment are roasting, baking, acid conditioning, acid curing and lime kiln. About one-half

of the domestic uranium mills pretreat ores by one or more of these five methods (fig. 12).

Uranium ores are roasted to convert vanadium to water-soluble vanadates and to destroy the slime-like character of the fines in the ores. The ores are roasted with salt in multiple-hearth furnaces at 825 to 850 degrees C. Calcines from the furnaces are ordinarily quenched in leach solutions to facilitate vanadium recovery (fig. 12). As roasting generally hampers the recovery of uranium by leaching, it is done only when the recovery of vanadium is desirable.

Baking of ores in multiple hearth furnaces, at temperatures of less than 500 degrees C., burns out car-





Explanation of letters on chart.

Operator	Mill location	Operator	Mill location
A Vanadium Corp. of America	Naturita, Colo.	J Vitro Uranium Co.	Salt Lake City, Utah
B Union Carbide Nuclear Co.	Rifle, Colo.	K The Anaconda Co.	Bluewater, N. M.
C Vanadium Corp. of America	Durango, Colo.	L Same	Same
D The Galigher Co.	Monticello, Utah	M Kerr-McGee Oil Industries, Inc.	Shiprock, N. M.
E Same	Same	N Same	Same
F Union Carbide Nuclear Co.	Uravan, Colo.	O Mines Development, Inc.	Edgemont, S. D.
G Same	Same	P Uranium Reduction Co.	Moab, Utah
H Same	Same	Q Rare Metals Corp. of America	Tuba City, Ariz.
H' Same	Same	R Trace Elements Corp.	Maybell, Colo.
H'' Same	Same	S Continental Uranium, Inc.	La Sal, Utah
I Climax Uranium Co.	Grand Junction, Colo.		
I' Same	Same		

FIGURE 12. Composite flowsheets of the principal elements of circuits in uranium mills in the western United States.

bonaceous material and increases the settling and filtering characteristics of small particles (Lennemann, 1956).

In acid conditioning, plant-waste acid liquors are mixed with ore to neutralize lime. Uranium and vanadium are precipitated by the addition of plant-waste basic liquors or ammonia and the ore goes through sand-slime separation.

Acid curing involves the preparation of a relatively dry mixture composed of sulfuric acid, water, and ura-

nium ore. The mixture is cured in storage piles for 6 to 8 hours to neutralize lime and solubilize vanadium for recovery in a water leach.

In the lime kill process, ore that contains more than 3 or 4 percent lime is given an initial acid leach in which up to 80 percent of the uranium in the ore is extracted. Uranium is recovered from the leach liquors in ion exchange columns. Uranium and vanadium in the solids are recovered by salt roasting and acid leaching.



**Leaching.** Uranium ores are leached in acid or carbonate solutions, or in water, to get uranium into solution so that it can be extracted by further chemical treatment. Easily filterable material is leached in percolation tanks; finely ground ores and those with high-slime or clay content are agitated during leaching and barren solids are separated after removal from leach tanks.

Acid leaching is the more commonly performed because ordinarily it is the most effective process. Ores with low-lime content are ground to about minus 35 mesh and mixed with sulfuric or hydrochloric acid and water to form a pulp composed of about 50 percent solids. If necessary, an oxidizing agent is added to the leach solutions to convert uranium to soluble compounds. Solutions that contain the uranium are called "pregnant solutions" which are separated from the pulp either by decanting or filtration.

Uranium ores that contain excessive lime (approximately 14 percent or more) are leached in carbonate solutions. Ore ground to about minus 65 mesh is mixed with sodium carbonate and water to form a pulp that is composed of 50 to 55 percent solids. The ore remains in contact with hot sodium carbonate solutions for several hours in pressurized autoclaves or up to 48 hours in open agitators. The pregnant solution is separated from the pulp by filtration.

Water leaching is employed to recover water-soluble vanadium after salt roasting or acid curing. Uranium is subsequently recovered by acid leaching or ion exchange.

**Liquid-Solid Separation.** Liquid-solid separation provides for the separation of barren solids from pregnant solutions before uranium is extracted from the solutions. Pulps from agitation leach tanks are separated into sand and slime fractions, then slimes are washed and decanted to obtain clear solutions. Clear solutions from percolation leach tanks are obtained through filter-bottomed leach tanks.

**Recovery of Uranium From Pregnant Solutions.** Uranium is recovered from pregnant solutions by chemical precipitation, extraction by ion exchange, or solvent extraction. Chemical precipitation caused by neutralization of the solution has been the most widely used process for solutions from acid and carbonate leach processes. The ion exchange method, however, is now used in many acid-leach plants, and more recently, a solvent extraction method has been developed for use in acid-leach circuits.

**Uranium Refining.** Uranium concentrates from some mills are further refined before they can meet A.E.C. specifications. In one method, low grade or impure concentrates are mixed with sodium carbonate, salt, and sawdust or fuel oil, then heated to about 950 degrees C. to reduce the concentrates to uranium dioxide and convert the impurities to water soluble sodium salts. Two other methods involve chemical digestion. In acid digestion, the low-grade concentrates are purified and neutralized with sodium carbonate to obtain a relatively pure solution of the uranium. The uranium is then precipitated from the solution by neutralizing with acid. Low-grade concentrates can also be treated by caustic

digestion in which a hot caustic wash dissolves all but the uranium.

## UTILIZATION

Prior to 1943, uranium-bearing ores were valued chiefly for their vanadium or radium content, and as late as 1939 there was a surplus of byproduct uranium from such ores. Since the development of the use of uranium for atomic energy, the U. S. Government has sharply curtailed its use for nonenergy purposes. Between 1943 and 1952 only 49,123 pounds of uranium oxide was consumed in the United States for nonenergy purposes as compared to an annual consumption of 200,000 pounds or more before 1943.

The principal nonenergy uses have been in ceramic products, luminescent paints, tool steels, and chemicals, but adequate substitutes have been found for most of these applications. In ceramic products uranium compounds are utilized to color pottery glazes and porcelain bodies, and to color glass. Uranium salts are combined in luminescent paints either for their own inherent fluorescence or as activators for other compounds in the paints. Uranium compounds have applications in special steels, photographic reagents, and as catalysts in organic chemical reactions.

Since 1945, most of the uranium consumed in the United States has been in the development and manufacture of atomic bombs and other nuclear weapons. Uranium is consumed also in the development of nuclear reactors for industrial power and nuclear propulsion for military equipment. Radio isotopes from reactors are receiving widespread application in medical research and therapy and as industrial tracers.

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## VANADIUM

BY MELVIN C. STINSON

Although vanadium is widely distributed in minute quantities through the crust of the earth, deposits of commercial value are rare. The greatest known concentrations of vanadium occur in Peru and the Colorado Plateau region of the United States.

Vanadates have been found in Kern and San Bernardino Counties, and some of the gold quartz veins of the Mother Lode in Amador and Calaveras Counties contain roscoelite, a vanadiferous micaceous mineral. However, vanadium has not been produced commercially from California deposits.

Most of the vanadium used in the United States is consumed as ferrovanadium in the manufacture of various types of steel. Vanadium is used mainly in steel for its grain-refining and alloying effects. Vanadium oxide and ammonium metavanadate are used as catalysts, in glass and ceramic glazes, for driers in paints and inks, and for laboratory research. Metallic vanadium has limited uses in special alloys.

*Mineralogy and Geologic Occurrence.* Vanadium is one of the more abundant trace elements and is very widespread through the crust of the earth. Although it ranks twenty-second in abundance among the elements in the earth's crust, in only a few places is it mined.

Vanadium is a grayish-white, nonmagnetic, metallic element with a high electrical resistivity. It is one of the least volatile metals at the melting point and is extremely difficult to reduce to the pure metallic state from its oxides.

About 70 vanadium minerals have been identified, but only five of them—patronite, bravoite, sylvanite, davidite, and roscoelite—are of primary origin. Of these, only patronite and roscoelite (which also occurs as a secondary mineral) are abundant enough to be considered as ore minerals.

The other known vanadium minerals are products of oxidation of primary vanadium-bearing minerals, and generally are very conspicuous because of their bright colors—green, yellow, red, orange and brown—and beautiful crystals. The most important of the secondary vanadium ore minerals are carnotite and vanadinite.

Patronite ( $V_2S_5 + nS$ ) is a vanadium sulfide with an excess of sulfur. It is found only at Mina Ragra, Peru, where it comprises the largest known vanadium deposit in the world. It is a greenish black amorphous mineral and generally contains some iron, nickel, molybdenum, phosphorus, and carbon.

Roscoelite ( $2K_2O \cdot 2Al_2O_3(Mg,Fe) \cdot O \cdot 3V_2O_5 \cdot 10SiO_2 \cdot 4H_2O$ ) is a vanadium-bearing mica found sparingly as a vein mineral in a number of rich gold-bearing veins, and in economically important quantities as a secondary mineral in the sandstones of Colorado and Utah. It is clove brown to greenish brown in color and carries about 20 percent  $V_2O_5$ .

Carnotite ( $K_2O \cdot 2UO_3 \cdot V_2O_5 \cdot nH_2O$ ) generally consists of an earthy aggregate of greenish-yellow or lemon yellow cryptocrystalline material. It is especially abundant in the plateau country of western and southwestern Colorado and adjacent areas in Utah, Arizona, Wyoming,

and New Mexico where it forms a cementing material in Jurassic sandstones (see section on uranium in this volume). It locally comprises pure masses that have replaced fossil logs and bones.

Vanadinite ( $Pb(PbCl)(V_2O_4)_3$ ) is a red, yellow, or brown mineral which occurs as crystalline, compact fibrous crusts in the oxidized zone of lead deposits. It is derived by the alteration of vanadiferous sulfides and silicates of the gangue and wall rocks.

Most rocks carry from a trace to a few hundredths of a percent of vanadium oxide. Coal ash may have a comparable content of vanadium oxide, and the vanadium oxide content of petroleum ash commonly is enough to be economically recoverable. The ash content of certain asphaltites, such as those in Argentina and Peru, become of economic importance when it is possible to use the asphaltite for fuel and to recover the ash for its vanadium content.

Magnetite iron ores contain as much as 1 percent vanadium oxide and, under favorable economic conditions, the vanadium could be recovered from the slag that is produced in smelting the iron ore. Ilmenite and other titanium minerals commonly contain 0.1 to 0.3 percent vanadium oxide which can be recovered during the extraction of the titanium. The phosphate rocks of Idaho and Montana contain from 0.11 to 0.45 percent vanadium oxide. The vanadium has been recovered during the manufacture of phosphoric acid and phosphate fertilizers.

Most of the world's production of vanadium has been from the vanadium sulfide deposits in Peru, the vanadium-bearing (carnotite) sandstones in the United States, and from the vanadate deposits in Northern Rhodesia and Southwest Africa.

The center of vanadium mining in the United States is in the northeastern part of the Colorado Plateau. Deposits of vanadium-bearing sandstone containing uranium are widely distributed in southwestern Colorado, southeastern Utah, northern Arizona, and northern New Mexico. Since 1954, some vanadium has been produced from South Dakota and Wyoming. Vanadium production in this region is a by-product of the uranium production. Most of the uranium-vanadium deposits of economic importance are found in the Shinarump conglomerate of Triassic age, and the Entrada sandstone and Morrison formation of Jurassic age. At many places the deposits are largely or wholly confined to a single stratigraphic zone in one of these formations. The ore minerals are roscoelite or carnotite, which generally occur as impregnations of the sandstone. Vanadium ore (roscoelite) of milling grade contains from 1 to 5 percent  $V_2O_5$ . A description of the carnotite deposits of the Colorado Plateau is included in the uranium section of this volume.

The Mina Ragra mine of the Vanadium Corporation of America is in the central part of the Peruvian highlands. This mine has been an important source of vanadium since 1907 when high-grade vanadium ore was first shipped to the United States. Mining operations were first started on outcroppings of high-grade oxide



ore. Shortly afterward a lenticular body of high-grade sulfide ore, containing the mineral patronite, was found under the oxides. This body, together with the oxide ore that bordered its upper part, was the source of the high-grade shipping ore exploited up to about 1925. The ore, made up of green and red vanadium oxides (the latter called hewettite), contained as much as 35 percent vanadium (Larsen and Welker, 1947, p. 9). Between 1907 and 1925, about 20,000,000 pounds of ore was shipped and averaged 20.5 percent vanadium (Larsen and Welker, 1947, p. 7). Surrounding the lens of high-grade vanadium oxides and sulfides are irregular concentric layers of other types and grades of ores. The layer next to the core consists of dark-green and dark-red altered shale containing replacements by calcium vanadates and averaging about 4 percent vanadium. Ore from this layer is being treated at a reduction plant on the property.

Vanadium mineralization in the Mina Ragra region is not confined to one deposit, but occurs in a north-trending zone about 125 miles in length. The vanadium is contained in a black, coal-like substance called asphaltite which has been intruded between and across the bedding of the shales to form lenses ranging from a few inches to several feet in thickness.

Many veins that contain lead, copper and zinc minerals also contain minor vanadium, especially in comparatively dry regions such as the southwestern United States, northern Mexico, Northern Rhodesia, Southwest Africa, or Spain.

The African vanadium ores contain vanadinite and desclorite and are mined at Broken Hill in Northern Rhodesia and from the vicinity of Otavi in Southwest Africa.

In California, vanadium minerals have been noted at several localities. Although the occurrence of vanadium minerals in San Bernardino County has been known for some time, principally in the Camp Signal district north of Goffs, no successful commercial recovery of vanadium has been made as yet. In the Camp Signal district, vanadium occurs as vanadinite and thin coatings of cupro-desclorite in the seams and cracks of quartz veins in granitic rocks. Two companies made unsuccessful efforts to recover these minerals (Wright, et al., 1953, p. 153). Layers of dark-green roscoelite as much as a half an inch in thickness, interlaminated with gold were found in Big Red Ravine, near the old Sutter Mill, but were destroyed to obtain the gold which was interlayered with it (Hanks, 1881, p. 428). Small quantities of vanadinite have been found in the Randsburg district of Kern County.

**Utilization.** Most of the vanadium used is consumed as ferrovanadium in manufacturing special steel and iron alloys. Other metals, particularly chromium and manganese commonly are constituents of such alloys. The presence of vanadium in steel increases its tensile strength without reducing ductility, and imparts toughness and torsional strength. In high-speed steels the vanadium content ranges from approximately 0.50 to 2.50 percent. Other alloy tool steels contain 0.20 to 1.00 percent and steels used for construction purposes generally contain from 0.10 to 0.25 percent vanadium. Most steels that contain more than 0.50 percent vanadium have special purposes.

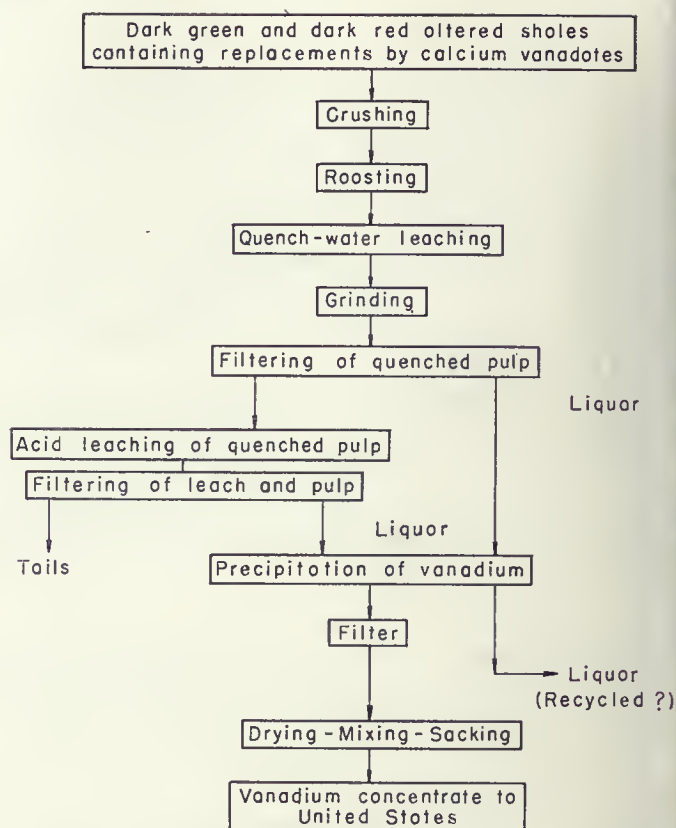


FIGURE 1. Flowsheet of Vanadium Corporation of America reduction plant at Jumasha, Peru. (Modified after Larsen and Welker.)

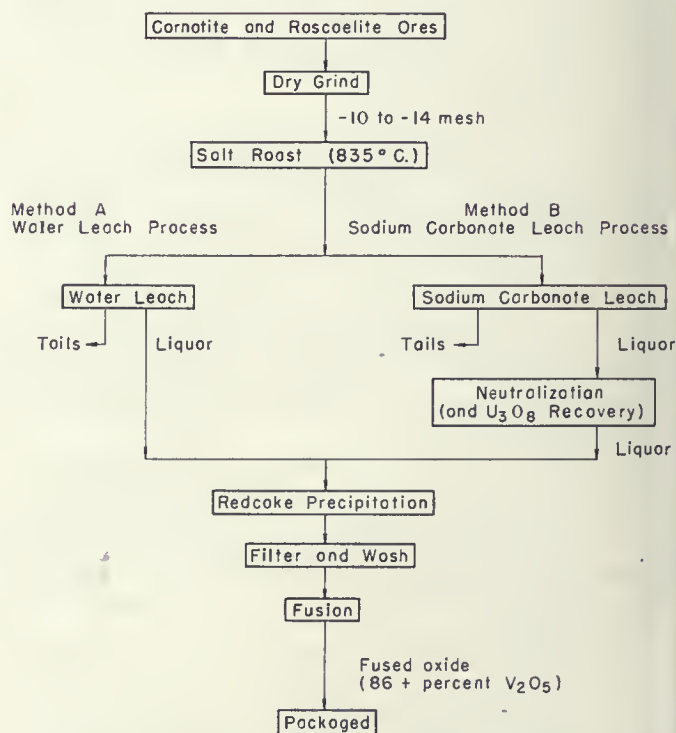


FIGURE 2. Flowsheet showing processes for recovery of vanadium from carnotite and roscoelite before 1948. (Modified after Lennemann.)



The alloy steels generally are made in open-hearth furnaces, the vanadium in the form of ferrovanadium being added shortly before casting. The addition of vanadium to the open hearth eliminates any oxides and nitrates that are present by forming compounds that go into the slag. Many special vanadium-bearing alloys are now made in electric furnaces. The chrome-vanadium series of alloy steels do not contain seams and surface imperfections commonly found in nickel steels. Several of these series of alloy steels are not face-hardened but develop a high resistance by heat treatment and are widely used for armor plate of medium thickness (Argall, 1943, p. 9).

The use of metallic vanadium is limited largely to alloying with gold in dental alloys, with copper and bronzes (such as for aircraft propeller bushings) and with aluminum for airframe construction (Davis, 1956, p. 4).

Vanadium in the form of ammonium metavanadate and sodium hexavanadate is used as a catalyst in the manufacture of sulfuric acid. To a minor extent, vanadium and its compounds are used in the glass, ceramic, dye, and chemical industries.

The present oversupply of by-product vanadium plus the extensive vanadium research in recent years should lead to new uses of vanadium.

**Methods of Treatment.** The vanadium-bearing ores shipped from Peru prior to 1925 averaged over 20 percent  $V_2O_5$  and needed no beneficiation before smelting. Since 1925, most of the Peruvian ore exported has required beneficiation before it can be used to charge electric furnaces. The ore, which averages about 4 percent vanadium, is treated by a combination roasting and leaching process. A water leach in a specially designed tank called a "quench box" is of special importance. Figure 1 is a generalized flowsheet of the process (1947).

Before 1948, the most used processes of vanadium recovery from carnotite or roscoelite ores of the Colorado Plateau, consisted of roasting the dry ground ore with 6 to 7 percent by weight of common salt. The calcine, obtained by roasting the salt and ore mixture, was quenched in water or sodium carbonate solutions to extract the vanadium which had been converted to a soluble sodium vanadate by the salt roast. Vanadium was recovered from the leach by adjusting the solution pH to 3 and then heating and stirring, which precipitated and flocculated a sodium polyvanadate, commonly called "red cake". The red cake was removed by filtration, washed and fused with a direct flame to obtain fused vanadium pentoxide containing more than 86 percent  $V_2O_5$  (Lennemann, 1956, p. 124). These processes are shown in figure 2.

The vanadium-bearing lead-copper-zinc ores of Northern Rhodesia are first treated by gravity concentration to recover 60-70 percent of the vanadium in a concentrate that contains 5 percent  $V_2O_5$ . The slimed minerals are then sulfidized and floated with emulsified fatty acids. A recovery of 90 percent of the  $V_2O_5$  is obtained from concentrates that contain 4 percent  $V_2O_5$ . The vanadium is finally recovered by leaching the concentrates in sulfuric acid. The pulp is neutralized with calcium hydroxide and heated with agitation to 60° C. The pulp is filtered and the vanadium-bearing filtrate treated by the

same process as that used on carnotite ore for the precipitation of red cake (Argall, 1943, p. 47).

In 1948, when the Atomic Energy Commission negotiated with the vanadium mills for the by-product uranium concentrate, flowsheets were expanded accordingly. Most of the early processes for the recovery of both uranium and vanadium involved a salt waste and either a water leach or a sodium carbonate leach to separate the soluble vanadium compounds from the insoluble uranium compounds. Some of the mills still recover vanadium and uranium by modifications of the salt roast process. Other mills are using more recently developed processes (see section on uranium in this volume). Still other mills recover only uranium from the carnotite type ores.

**Markets.** For many years vanadium ore was quoted at 27½ cents a pound of contained  $V_2O_5$ , but on March 8, 1951, the price was advanced to 31 cents. This quotation, however, disregards penalties based on grade of the ore or the presence of objectionable impurities—matters important to the refiners, inasmuch as impurities vitally affect recovery (Davis, 1956, p. 3).

Engineering and Mining Journal Metal and Mineral Markets during the first half of 1956 quoted vanadium metal at \$3.45 per pound in 100 pound lots. Ferrovanadium was quoted as follows: Per pound contained vanadium; carload lots, various sizes, packaged, f.o.b. destination continental U. S., (50-55 percent vanadium); open hearth \$3.10, Crucible, \$3.20, and high speed, \$3.30

According to a recent article (The Mining Record, Sept. 6, 1956, p. 5) the Gibraltar Uranium Corporation of Denver, Colorado has developed a market for vanadium concentrates in Europe, particularly in Germany and Austria. The Gibraltar Uranium Corporation will buy vanadium liquor that has been separated out in the uranium processing, from the Kerr-McGee processing plant at Shiprock, New Mexico. The proposed operations call for the shipment of 125,000 pounds of vanadium concentrates per month.

Most of the vanadium used in the steel industry is consumed in the eastern United States. A California vanadium producer would have to be able to mine and concentrate his vanadium ore cheaply enough to compete with by-product vanadium from the uranium mills on the Colorado Plateau. California vanadium ore to be of commercial significance would have to be either cheaply mined on a large-scale basis or recovered as a by-product of base metal operations.

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## WOLLASTONITE

By BENNIE W. TROXEL

Wollastonite, a new mineral in the nonmetallic field, has many potential applications, particularly in the ceramic, chemical, and paint industries. Although very large deposits of wollastonite exist in California, in 1955 no continuous mining operations had developed.

**Mineralogy and General Geology.** Wollastonite is a calcium metasilicate ( $\text{CaO} \cdot \text{SiO}_2$ ) with a theoretical chemical composition of 48.3 percent CaO and 51.7 percent  $\text{SiO}_2$ . It is triclinic and is nearly identical in physical properties with parawollastonite, which is monoclinic. It fuses at  $1540^\circ \text{C}$ . after inversion at  $1150^\circ \text{C}$ . to pseudowollastonite which is pseudo-hexagonal and probably monoclinic. Some mineralogists refer to the low temperature form as beta wollastonite and to the high temperature form as alpha wollastonite.

Wollastonite commonly contains as much as several percent manganese, iron, or magnesium oxides. It has a hardness of 4.5 to 5 on Mohs' scale and ranges in specific gravity from 2.8 to 2.9. It is generally fibrous, brittle, white to cream colored or gray, translucent, and has one perfect cleavage and two good cleavages. It is decomposed by hydrochloric acid.

Wollastonite ordinarily occurs in impure limestone that has been metamorphosed near igneous intrusive bodies, and commonly is associated with diopside, idocrase, garnet, epidote, calcite, and quartz. These minerals ordinarily must be removed before wollastonite can be used in ceramic bodies.

Wollastonite is abundant in many areas throughout the world, but only at a locality near Willsboro, New York (Amberg and McMahon, 1949) and a locality north of Randsburg, California (Thorndyke, 1936) has it been mined commercially. The wollastonite at Willsboro occurs in a west-northwest trending belt of pre-Cambrian metamorphic rocks. Two wollastonite-bearing layers appear to contain most of the material of commercial interest. The one that has been mined to date is 40 to 45 feet in average width, extends along the surface for at least 2,000 feet, and is estimated to contain at least 3 million tons of wollastonite-bearing rock. Associated with the wollastonite are layers rich in andradite garnet, as much as 8 inches thick, and thinner layers rich in magnetic green diopside.

Since 1947, research pertaining to the milling, beneficiation, and utilization of wollastonite from the Willsboro deposit has been undertaken by the New York State College of Ceramics and Godfrey L. Cabot, Inc., White Pigments Division, Boston, Massachusetts. Cabot, Inc. constructed a beneficiation plant and mill and is now marketing ground wollastonite in several size ranges. The material is ground and treated magnetically to yield nearly pure wollastonite (75 percent), garnet (15 percent) and waste (10 percent).

**Occurrences in California.** Of the 35 occurrences of wollastonite in California, reported in Bulletin 136 of the California Division of Mines (Murdoch and Webb, 1948) only a few appear to be capable of yielding commercial quantities of the relatively pure mineral. Most of the wollastonite in California occurs in areas where

impure limestone of Lower Mesozoic or Upper Paleozoic age is near intrusive bodies of granite or other acidic igneous rocks of Mesozoic age. This type of terrane is common in the desert areas of the south and southeastern parts of the state and in the Sierra Nevada.

In the Big Maria Mountains, 16 miles northwest of Blythe, eastern Riverside County, pods of high-purity wollastonite occur in crystalline limestone in the lower part of the Paleozoic (?) Maria formation. The pods range from a few inches in maximum dimension to as much as 1,800 feet in length. The largest body appears to be the core of a shallow anticline that plunges west-northwest. Mixed metamorphic rocks stratigraphically beneath the crystalline limestone also contain wollastonite-bearing layers. These rocks appear to be as much as 500 feet thick and can be traced laterally for about 4 miles. The wollastonite-bearing rock in both zones is fine-grained and is interbedded with fine-grained diopside and thin layers of crystalline limestone. The individual layers of wollastonite in this succession of rocks vary in purity. Local beds are brownish-gray and appear to have a relatively high iron content. A few tons of nearly white wollastonite have been mined from similar wollastonite-bearing rocks in the Little Maria Mountains. In 1956, the deposits in both the Big Maria and the Little Maria Mountains were being developed by California Limestone Products with offices in Beverly Hills, California.

White, coarsely crystalline wollastonite occurs in Permian limestone in Warm Spring Canyon on the east slope of the Panamint Range, Inyo County, California. The largest body is an elongate lens about 750 feet long and 35 feet in average thickness. Most of the rock in the lens consists almost wholly of wollastonite but siliceous and calcareous material forms local layers and irregular masses. Diopside, quartz, and calcite are minor constituents throughout the lens of wollastonite.

Wollastonite-bearing metasedimentary rocks of probable Paleozoic age also occur near Code Siding, north of Randsburg in Kern County. They are exposed in three low mounds near the center of a small valley in the northeastern part of El Paso Mountains. In these rocks the wollastonite occurs as numerous coarse- to fine-crystalline gray layers interstratified with nearly equal or greater amounts of fine-grained gray diopside and buff to tan massive garnet. The sequence is several tens of feet in total thickness. The rocks are intricately folded and trend northward. The extent of this deposit is not known because it extends beneath alluvium. In 1933-34 this deposit yielded an undisclosed amount of material for the manufacture of mineral wool. This was the first commercial production of wollastonite in the United States, if not in the world.

The western part of the Shadow Mountains, 22 miles northwest of Victorville, San Bernardino County, is underlain by metamorphosed rocks that contain wollastonite. A north-striking, east-dipping succession of layered metamorphic rocks composed mostly of schist, marble, and hornfels of probable Paleozoic age, is exposed in a group of low hills about 1 mile long. One bed, about 15



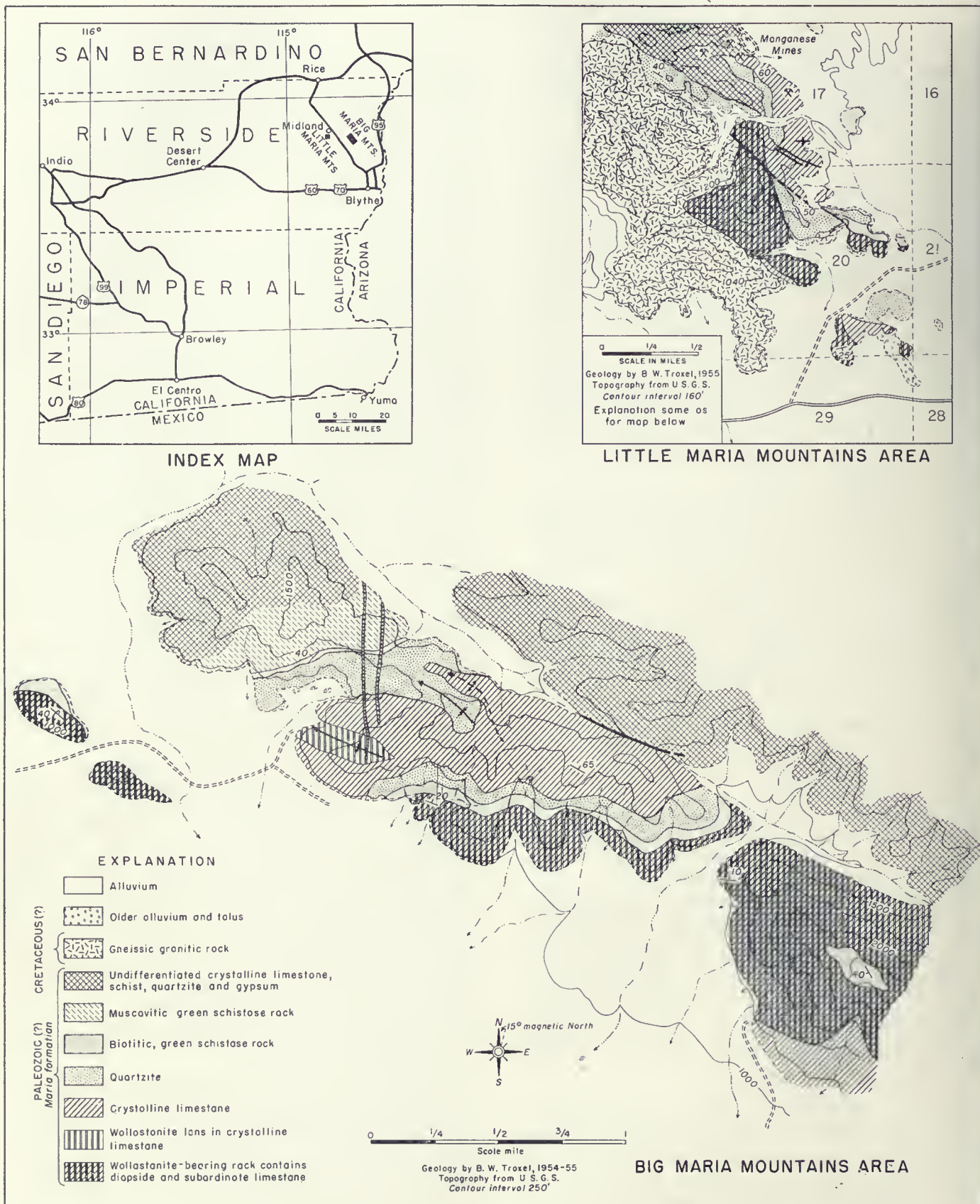


FIGURE 1. Generalized geologic maps of wollastonite-bearing rocks of the Little Maria and Big Maria Mountains.





FIGURE 2. View northeastward toward part of the southwestern flank of Big Maria Mountains from Blythe-Midland road about 3 miles distant. Dark-colored layered rocks extending to right from center of photograph are thick succession of wollastonite-bearing metasedimentary rocks.

feet thick, is composed of coarsely crystalline fibrous gray wollastonite, dense gray diopside and idocrase, and pale brown massive garnet. Wollastonite locally comprises more than 40 percent of the rock.

Several wollastonite occurrences also have been reported in crystalline limestone in other parts of the Mojave Desert, principally near Barstow and Victorville, and near Big Bear Lake. Still other wollastonite deposits exist throughout the Sierra Nevada where the mineral has been found in metamorphosed limestone especially in the vicinity of tungsten deposits. Wollastonite also occurs in metasedimentary rocks near Darwin, Inyo County, and has been noted in the north part of the Argus Range almost due east of Darwin.

Limestone in roof pendants of metasedimentary rocks (Upper Paleozoic-Lower Triassic?) in the eastern part of San Diego County, and the western part of Imperial County, contain small amounts of wollastonite, none of commercial importance. Wollastonite has been found in the eastern part of the Cargo Muecho Mountains, southeastern Imperial County.

**Physical and Chemical Properties.** The physical and chemical properties of wollastonite show virtually no differences from deposit to deposit. It is brittle, fibrous even in very small particles, grinds white, and is chemically inert. In comparison with most other extenders, wollastonite shows a low water and latex adsorption in the same ratio that it shows lower oil adsorption (G. J. Duffy, personal communication, 1956). It is easily separated from magnetic minerals that commonly occur with it, but separated with difficulty from calcite, quartz, and non-magnetic diopside. These minerals need not be removed for certain applications of wollastonite.

Wollastonite fires white to gray, matures at a slightly lower firing temperature than most conventional ceramic bodies and can be fired at a faster rate. It has a low firing range (cone 06 to cone 5), and certain wollastonite bodies can be fired along with the glazes, thus eliminat-

ing second firings. Ceramic bodies that contain wollastonite have low shrinkage values, high modulus of rupture, high thermal shock resistance, and high porosity. Wollastonite bodies can be vitrified if desired. Fired wollastonite bodies do not warp as much as conventional bodies and the fibrous structure imparts a high mechanical strength (Amberg, et al., 1949). With proper formulation of glazes, a satisfactory glaze can be obtained on high-wollastonite bodies without the application of an engobe (G. J. Duffy, personal communication, 1956). Fired bodies that contain wollastonite have high dielectric strength and low electrical loss (Neely, 1954).

Bonded and baked bodies that contain wollastonite can be worked with ordinary tools. The material can be sawed and drilled nearly as easily as wood and holds nails and screws well.

**Uses.** Many uses have been suggested both for crude and beneficiated wollastonite, and subsequent research has proved that the mineral can be used successfully in the ceramic industries, as a nonmetallic filler, and for numerous miscellaneous applications. These are mostly potential uses where acceptance will depend largely on the readiness of certain mineral-consuming concerns to use wollastonite as a substitute for other materials, some of which may not be as desirable as wollastonite, but are less expensive. It commonly could be substituted in some of the uses to which such materials as clay, limestone, steatite, asbestos, serpentine, fibrous tale, and flint-limestone mixtures are put. For some uses it may become a material for which no satisfactory substitute exists.

In the ceramic industry, beneficiated wollastonite has proved satisfactory for use in floor and wall tile bodies, in porcelain fixtures, thermal insulation products, acoustical tile, frits for enamelware, glazes, dinnerware, and electrical insulator products (Amberg and McMahon, 1949). This is attributable principally to the light color after firing, low shrinkage values, low warping values and, for electrical products, to its low electrical loss.

As a paint extender wollastonite is useful because it absorbs less oil than most extenders, holds pigments at lighter, has less viscous consistency and is more wettable than fibrous tale. Less absorption of oil results in savings to paint producers. The fibrous particles tend to interlock, thereby improving the toughness and durability of paint.

Wollastonite is suitable as a filler in asphalt-based floor tiles. In certain floor tiles that contain serpentine and asbestos fillers, a superior product was obtained when fibrous wollastonite was substituted for serpentine, even when less asbestos fiber was used (Amberg and McMahon, 1949, p. 36).

Wollastonite is used in welding rod coatings and makes an excellent white mineral wool. It has certain applications as coating and filler for paper, as an abrasive, a bond for abrasive wheels, as filler for plastics and cement, and as a filter. Bonded and baked wollastonite products could be used for wall board and exterior sheathing.

**Mining, Processing, and Marketing.** Only the wollastonite deposits that are large enough to be mined from open pits at the surface have been mined to date, but Cabot, Inc. will probably mine underground by 1958







(G. J. Duffy, personal communication, 1956). Cost of transportation to markets limits the utilization of deposits in remote areas.

Mining costs of California wollastonite deposits may be slightly higher than for ceramic materials of similar uses because of the extreme toughness of the wollastonite-bearing rock in some deposits. This toughness is created by the tight interlocking of small crystals. However, overall costs of open-pit mining of wollastonite might be lower than underground methods of recovery of certain ceramic materials, such as talc.

Wollastonite can be ground and sized by standard methods but the toughness of some types makes milling costly. Beneficiation, if needed, and grinding may be done with standard equipment such as magnetic separators, wet pebble mills and classifiers. Crushing can be accomplished with ordinary jaw and spring crushers, and rolls. Grinding techniques can be varied to control acicularity of the wollastonite particles.

In mid-1956 large tonnage markets for wollastonite in California had yet to be developed. New York wollastonite has been available in California since 1953 and a few tens of tons have been consumed annually in the state as a raw material in ceramic glazes.

In 1956 ground and bagged New York wollastonite retailed in carload lots at prices ranging from \$19 for minus 20 mesh to \$39.50 for minus 325 mesh per ton, f.o.b., New York. Shipping charges were about \$30 per ton in 50-ton carloads from New York to the west coast.

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FIGURE 4. View westward of part of the principal wollastonite body in Warm Spring Canyon. Wollastonite underlies rough outcrops near base of hill in foreground. High part of Panamint Range in distant background.



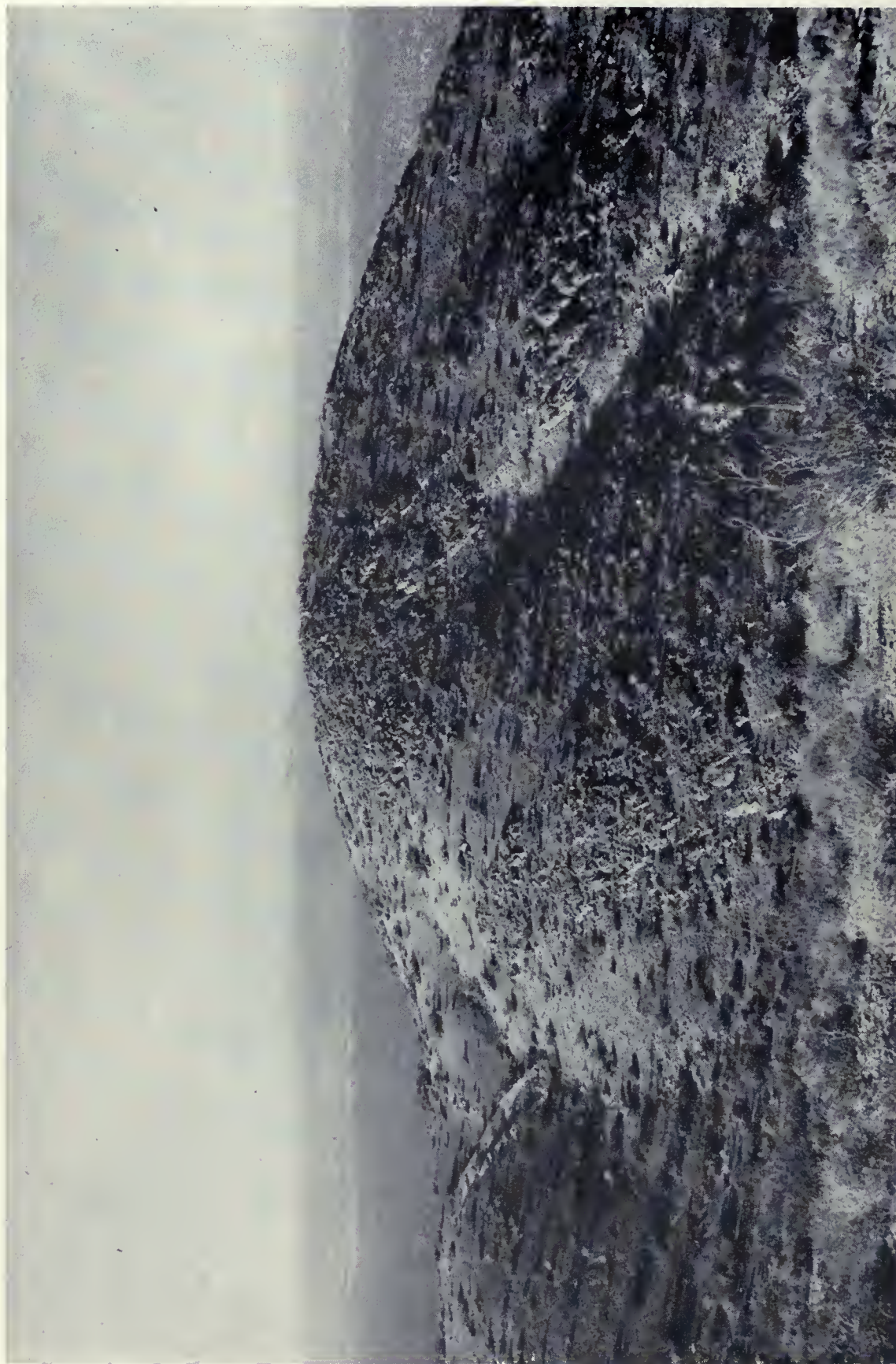


FIGURE 5. Wollastonite-bearing rocks in western part of the Shadow Mountains, western San Bernardino County. Rough-surfaced rocks at crest of hill are composed of layers of garnet, epidote, wollastonite, and calcite, and are about 40 feet wide. View is to north.



## ZINC

BY J. C. O'BRIEN

The zinc produced in California has been obtained largely from two sources: (1) mines in the desert regions of eastern California that are also sources of lead and silver, and (2) copper-bearing deposits of the Sierran foothill belt and Shasta County. Since the first recorded production of zinc in 1906, approximately half of the state's total output of about 190 million pounds was obtained during the periods of relatively high prices induced by World Wars I and II. With less favorable price conditions, zinc production in the state has declined or stopped completely. In 1954, California production was 1,310 short tons valued at \$288,200 compared to 5,300 short tons valued at \$1,155,400 in 1953. The decrease is attributable to the fact that the Darwin and Shoshone groups in Inyo County were idle for most of the year. The average price of zinc in 1954 was 10.68 cents per pound compared to 10.85 cents per pound in 1953.

**Mineralogy.** Sphalerite ( $\text{ZnS}$ ), the only important primary ore of zinc, is present in nearly all types of sulfide deposits. It is pale yellow to black depending on the amount of iron present. The usual color is yellowish brown to reddish brown. It has a very prominent cleavage and a resinous luster. Pure sphalerite contains 67.0 percent zinc. Marmatite, ferriferous sphalerite containing 10 percent or more iron, is a common zinc mineral in the Shasta copper belt. It is black and commonly fine-grained and in many places occurs as streaks and layers giving the ore a banded appearance. Sphalerite commonly oxidizes to smithsonite which is relatively insoluble, but, in the presence of dilute sulfuric acid, sphalerite is dissolved and may not be redeposited. Instead, the zinc may be dispersed in the ground water as a sulfate. Many deposits have been leached of their zinc content. Carbonate rocks, however, act as a precipitant for descending zinc solutions and in this environment bodies of zinc carbonate and silicate ordinarily form below oxidizing lead deposits. Smithsonite ( $\text{ZnCO}_3$ ) is the most common of the oxidized zinc minerals, but hemimorphite (calamine) ( $\text{H}_2\text{Zn}_2\text{SiO}_5$ ) is also of commercial importance. Smithsonite is commonly white with a vitreous luster. It is sometimes blue or green resembling chrysocolla but it is heavier and harder. Calamine can be distinguished from smithsonite by its cleavage which is parallel to the length of the crystals.

**Geologic Occurrences.** Zinc and lead minerals ordinarily occur in close association and most of the world's output of zinc has been obtained from deposits similar to those described in the section on lead in this volume. Zinc and copper minerals are also commonly associated and typical zinc-copper deposits are described in the copper section.

Replacement deposits are the principal sources of the world's zinc, but zinc mineralization is common also in fissure veins and other types of cavity fillings. Deposits of the world's greatest zinc district near Joplin, Missouri, represent selective hydrothermal deposition in Paleozoic limestone and dolomite.

The principal zinc-bearing deposits in California are confined largely to two metallogenic provinces. One is the copper-zinc belt which extends from Fresno County along the Sierran foothills to include districts in the Klamath Mountains of Shasta County. The other includes the lead-silver-zinc districts of the east-central portion of the state.

The copper-zinc mines have contributed most of the state's total zinc production to date. The principal sources of zinc in Shasta County have been the Afterthought, Balaklala, Bully Hill, Richmond, Mammoth and Rising Star mines. In the Sierran foothills, the most important producers of zinc have been the Big Bend mine, Butte County; the Penn, Quail Hill, and Napoleon mines, Calaveras County; and the Blue Moon mine, Mariposa County. The lead-zinc-silver mines described in the section on lead in this bulletin were the first important producers of zinc in California. Since 1948, they have been the leading producers and since 1954, the only source of zinc in California. The Cerro Gordo mine east of Lone Pine was a significant source of zinc from 1911 to 1916. The zinc ore, consisting essentially of the carbonate, smithsonite, was mined largely after the depletion of the known reserves of the lead-silver ore. On the 400 foot level of this mine, a pipe of carbonate ore 5 feet in diameter and 150 feet long averaged more than 40 percent zinc. The zinc ore shipped from the Cerro Gordo mine prior to January 1, 1913, amounted to 10,000 tons which averaged 35 percent zinc. The total production figures, however, are not available. There has been no production recorded from this mine since 1916.

Since 1948, the Darwin and Shoshone group of mines in the Coso and Teeopa districts of Inyo County have been the principal producers of zinc in California. In these districts, zinc is a by-product of lead-silver ores which contain small amounts of sphalerite and smithsonite. The ore bodies in the Coso district occur as replacements of silicated limestone rocks, as bedded replacements, or as fissure fillings (Davis and Peterson, 1949, p. 137). The mill heads average approximately 7.5 percent lead, 7.5 percent zinc and 5 ounces of silver per ton. The ore bodies of the Coso and Cerro Gordo districts were formed in Paleozoic rocks and their geological features are summarized in the section on lead in this bulletin. The ore bodies in the Teeopa district are replacements and fissure fillings in a fault zone in dolomite. Lead-zinc mineralization has also taken place in the Resting Springs, Trona, Panamint, Ubehebe and Wildrose districts of Inyo County.

Some zinc ore has also been shipped from the Carbonate King and Mohawk mines in the Clark Mountain district, San Bernardino County. In July and August 1950, 110 tons of ore assaying 40 percent zinc were shipped from the Carbonate King mine to Tooele, Utah. The operators of the Mohawk mine reported that 640 tons of ore shipped to Selby between May and December 1951, averaged 8 to 10 percent lead, 3 percent zinc, and 7 to 8 ounces of silver per ton (Wright et al., 1953, pp. 106, 111). In this area, as in Inyo County, most of the lead-silver-zinc deposits occur along fractures in limestone.





FIGURE 1. Map showing location of mines which have been the principal zinc producers in California.





FIGURE 2. Afterthought mine of the Coronado Copper and Zinc Company—flotation plant and mine shops. November 1948.

Small amounts of zinc have also been shipped from the Silverado district of Orange County, the Mineral King district of Tulare County, and Santa Catalina Island, Los Angeles County. In the Silverado district, veins containing silver-bearing galena, sphalerite, and pyrite have formed in metamorphic rocks. The deposits in the Mineral King district contain chalcopyrite, pyrrhotite, pyrite, arsenopyrite, sphalerite and galena, and occur along contacts between limestone and slate or granite.

**History.** Although sphalerite and smithsonite had been noted in the lead mines of Inyo County and Santa Catalina Island as early as 1884, the first production of zinc in California was not recorded until 1906. In that year, 206,000 pounds of zinc valued at \$12,566 was produced but it was tabulated as unapportioned. In 1907, large bodies of smithsonite were found in the footwall of the old lead stopes in the Cerro Gordo mine in Inyo County and 144,213 pounds of zinc valued at \$8,598

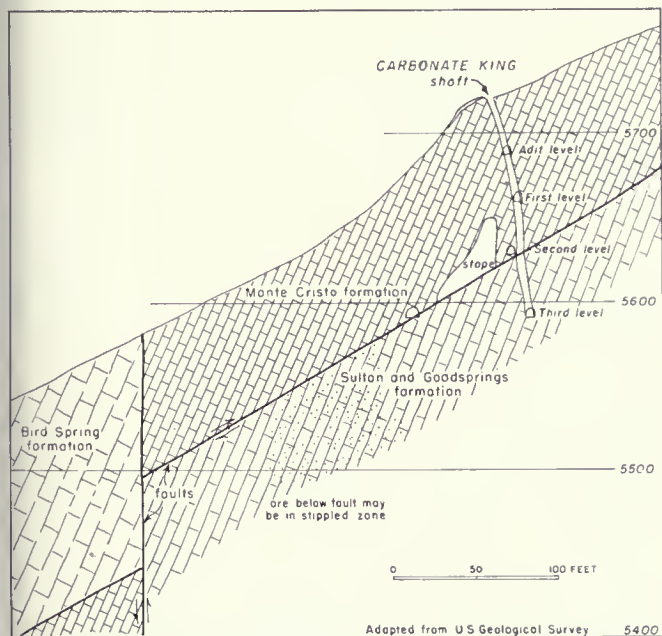


FIGURE 3. Geologic section through the Carbonate King zinc mine, Koko Weef Mountains, San Bernardino County. Reprinted from *California Journal of Mines and Geology*, vol. 49, no. 1.

were shipped from the county in that year. A production of 33,546 pounds of zinc from Orange County was also reported in 1907.

A relatively large amount of zinc carbonate ore had been shipped from Inyo County before zinc was recovered from the sphalerite that is associated with the copper ores in Shasta County. Zinc, although long recognized as a prominent constituent of numerous copper deposits in Shasta County, was a detrimental material in the smelting of copper ores. Ore bodies rich in zinc were left unmined prior to 1915. In that year, the General Electric Company built a small experimental electrolytic zinc plant at Winthrop and recovered 300 to 400 pounds of zinc per day. In 1917 and 1918, electrolytic zinc was produced from smelter fumes by the Mammoth Copper Company at Kennett. In 1918, electrolytic zinc was produced at Winthrop from raw ores mined at the Afterthought and Bully Hill mines. When the average price of zinc declined from 14.2 cents per pound in 1915 to 7.3 cents per pound in 1919, the electrolytic plants were closed down.

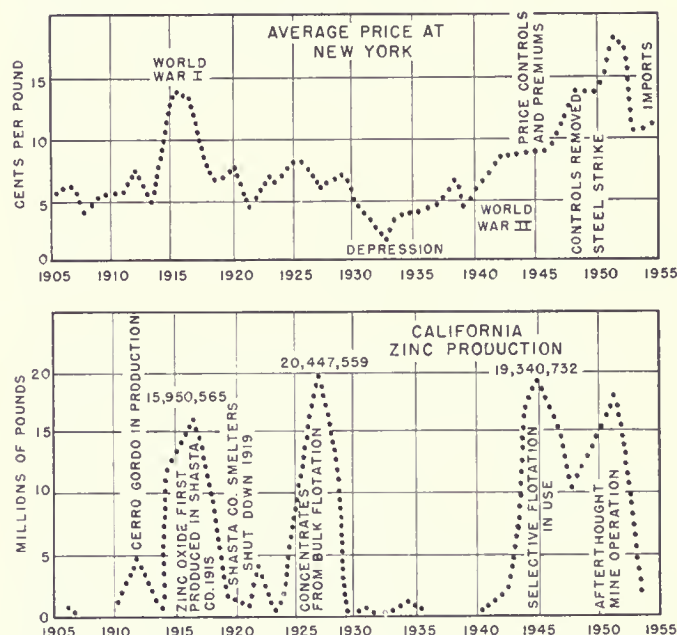


FIGURE 4. Chart showing production of zinc in California and the price of zinc in the United States.

In 1917, the Bully Hill Mining Company built a 150-ton flotation plant at Winthrop but it was unsuccessful, as was a 300-ton flotation plant built by the Afterthought Mining Company at Ingot in 1918. Copper concentrates at the Ingot plant carried 12 percent zinc and the zinc concentrate carried 2.6 percent copper. At Bully Hill, the Shasta Zinc Company built a reverberatory furnace and a zinc oxide plant which was operated from June to December 1922, when it was shut down because of a drop in the price of zinc oxide.

In 1924, when the California Zinc Company took over the operation of the Afterthought and Bully Hill mines, the smelting operation and the production of zinc oxide were discontinued. The flotation plant was remodeled and a bulk concentrate containing 43 to 49 percent zinc, about 4 percent copper, 7 to 11 percent iron, 1.3 to 1.7



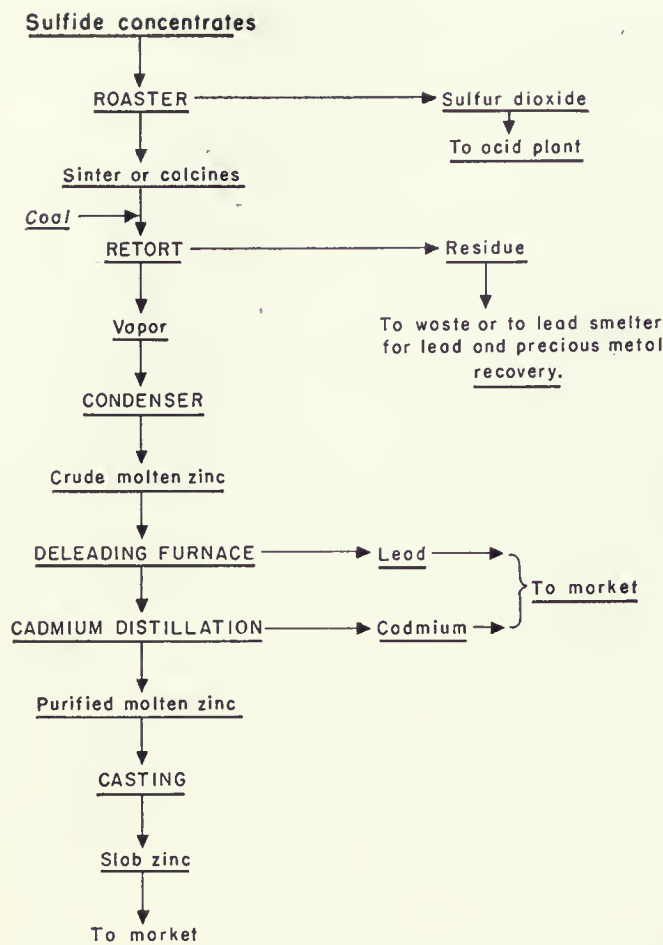


FIGURE 5. Typical flow sheet of a horizontal retort zinc smelter.

percent lead and 2.3 percent silica was obtained (Logan, 1926, p. 376). This concentrate was shipped to Belgium for treatment.

In December 1925, a flotation plant was put into operation at White's Landing on Santa Catalina Island, Los Angeles County, to treat the lead-zinc ores mined at the nearby Black Jack and Quarry mines. A novel feature at this plant was the use of salt water pumped from the ocean (Tucker, 1927, p. 38). The ore, which occurred in veins within hornblende schist, contained from 7.2 to 8.7 percent zinc, 1.5 percent lead, and 3.5 ounces of silver per ton. The zinc concentrates contained 45 percent zinc, 3.2 percent lead, and 11.5 ounces of silver per ton, and the lead concentrate contained 55 percent lead, 8 percent zinc, and 93 ounces of silver per ton. Mill tailing contained 2 percent zinc, 0.2 percent lead, and 0.9 ounce of silver per ton. The zinc concentrate was shipped to Belgium and the lead concentrate to Selby, California.

The price of zinc dropped from 7.337 cents per pound in 1926 to 6.242 cents per pound in 1927, and the shipment of zinc concentrate to Belgium was no longer profitable. The zinc-copper mines of Shasta County closed in August 1927, and the Santa Catalina properties closed early in 1928. Except for flotation concentrate, made as a by-product from the gold ore treated at the Spanish mine in Nevada County in 1931, California's production

of zinc from 1928 to 1943 came from the carbonate ores of Inyo, Orange, and San Bernardino Counties.

The federal government's plan for the use of premium payments to increase the output of strategic minerals went into effect in 1942. Loans were made available to develop and mine deposits of needed minerals. The number of California zinc producers increased from four in 1942 to ten in 1943, and by 1945, selective flotation plants with a combined capacity of 800 tons per day were concentrating ores from the Big Bend mine in Butte County, the Penn mine in Calaveras County, the Richmond mine in Shasta County, and the Blue Moon mine in Mariposa County (Bramel, 1948, p. 163). Zinc production rose from 16,390 pounds in 1939 to 19,340,732 pounds in 1945 and came from 12 mines in eight counties. The production was far in excess of the development of reserves however, and by the end of 1945, both the Big Bend and Blue Moon mines were shut down. The flotation plant at the Richmond mine operated until June 30, 1947, when the premium payments were stopped and the developed ore was exhausted. Zinc production dropped to 5,325 short tons in 1948 but increased to 7,209 tons in 1949 because of concentrates produced at the new flotation plant built by the Coronado Copper and Zinc Company at the Afterthought mine in Shasta County. This operation was closed in July 1949 when the price of zinc, copper, and lead declined, but it was resumed a year later and continued until August 1952. The production of zinc in California has exceeded a million pounds each year since 1942. In 1954, zinc production was estimated at 2,620,000 pounds valued at \$288,200.

*Mining and Concentrating Processes.* All of the California zinc deposits are mined by underground methods. Some of the carbonate ores of Inyo, Orange and San Bernardino Counties were rich enough to ship to smelters without milling. All of the sulfide ores, however, contain pyrite, and the zinc minerals are so intimately associated with either chalcopyrite or galena that they require costly fine grinding before they can be separated. A lead-copper and a zinc concentrate are obtained by selective flotation. A description of mining methods and the selective flotation process is included in the chapter on copper.

*Metallurgy.* Elemental zinc is removed from its ores by two common processes: (1) the retort or distillation process, and (2) the electrolytic process. The distillation process is the most widely used. It was the only commercial method known and in use until 1915 when the electrolytic process was developed and put on a commercial basis. In preparation for either process, the ore or concentrate must be roasted to remove the sulfur and to produce a zinc oxide called calcine. Roasting is commonly done in a circular multiple-hearth roaster of the McDougall type in which the concentrate is fed in at the top and falls from hearth to hearth through the hot ascending gases. The furnace is commonly fired with natural gas but fuel oil or powdered coal is sometimes used. Concentrates carry enough sulfur to support combustion once started. In the recently developed fluosolid process, roasting is done in a brick-lined roaster having a perforated bottom through which air is blown to keep the material in suspension. The burning concentrates



boil and churn like a fluid and the temperature and oxidation can be closely controlled by regulating the feed and the air pressure.

Calceines to be treated by the distilling process are usually sintered to reduce their sulfur content further for it is estimated that each unit of sulfur left in the calcine will hold back two units of zinc from distilling. Sintering consists of burning the calceines to incipient fusion by passing hot air through the bed of calceines as it is drawn through a furnace on a series of metal pans. The sulfur content can be reduced to as low as 0.25 percent by sintering. Flue dust carried by the gases from the roasting and sintering processes is collected in dust chambers, cyclone separators, and Cottrell precipitators. The sulfur compounds produced in the roasting and sintering processes are used for the production of sulfuric acid.

The horizontal distillation process was the only process used until 1925 when the continuous vertical-retort process was developed commercially. For either the horizontal or vertical-retort process, the calcine or sinter is ground and mixed with 40 to 60 percent of powdered coal. In the horizontal-retort process, this mixture is charged into clay retorts about 8 inches in diameter and up to 6 feet in length. Fire-clay condensers are fastened to the ends of the retorts and metal extensions called prolongs are fitted to the ends of the condensers. Double banks of these retorts are placed in a combustion chamber and externally heated with natural gas, producer gas, oil or pulverized coal. The furnace cycle usually takes 24 hours of which 18 to 20 hours are for the actual distillation. Liquid zinc is collected in the condensers and amounts to about 90 percent of the metal charged. Additional zinc is recovered as zinc oxide and flue dust.

In the continuous vertical-retort process, the sintered calceines are ground and mixed with coking coal and a small amount of an organic binder and briquetted. The briquettes are dried and charged into the top of vertical muffle furnaces. Heat is applied to the sides of the furnace and metallic zinc vapor and other gases are taken off near the top of the furnace. The zinc vapor is condensed and cast into slabs and called spelter. Cadmium and lead are condensed with the spelter. Zinc is refined and separated from lead, cadmium and other metals by successive stages of distillation and condensation. In the New Jersey refining process, spelter is melted in a pot at the bottom of what is called the "lead column." The molten zinc flows downward over a series of trays counter to an ascending column of metallic vapors. The zinc vapor is condensed at the top of the lead column and flows into the "cadmium column." Cadmium is condensed as a dust or as a cadmium-zinc alloy at the top of the "cadmium column." Refined zinc is drawn off beneath the cadmium and lead, and zinc-iron dross settles by gravity to the bottom of the pot. A metal containing 99.99 percent zinc can be obtained by this method.

Much zinc is now recovered in fuming plants treating old lead blast-furnace slags containing zinc. A mixture of molten and solid slag is fed into the top of a furnace and a blast of pulverized coal and air is blown through the molten mass from the bottom. The zinc is volatilized and recovered as zinc oxide in flue chambers and bag-

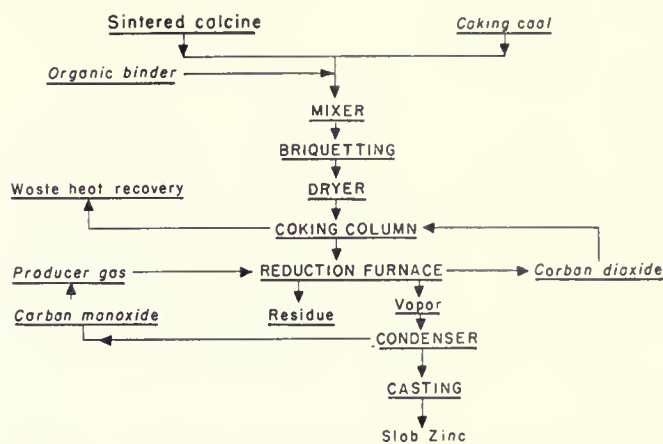


FIGURE 6. Flow sheet of fuel-fired vertical retort zinc smelter.

houses. The zinc oxide must be treated further by the electrolytic process or by deleading in a rotary kiln.

In the electrolytic process, the zinc calcine is leached with dilute sulfuric acid and the contained metals are put into solution as sulfates. The solution is neutralized with powdered limestone and manganese dioxide is added. Iron is precipitated and filtered out. Gypsum is a byproduct. The filtrate is agitated with zinc dust in a pachuca tank and any antimony, alumina, copper, nickel, cadmium, or germanium present is precipitated and filtered out. The purified zinc sulfate solution is fed into lead-lined tanks in which lead anodes and aluminum cathodes are suspended. The direct current applied varies from 30 to 100 amperes per square foot of the aluminum cathode surface on which the zinc is deposited. The zinc is stripped from the cathodes when it is about  $\frac{3}{16}$ -inch thick and is melted and cast into slabs.

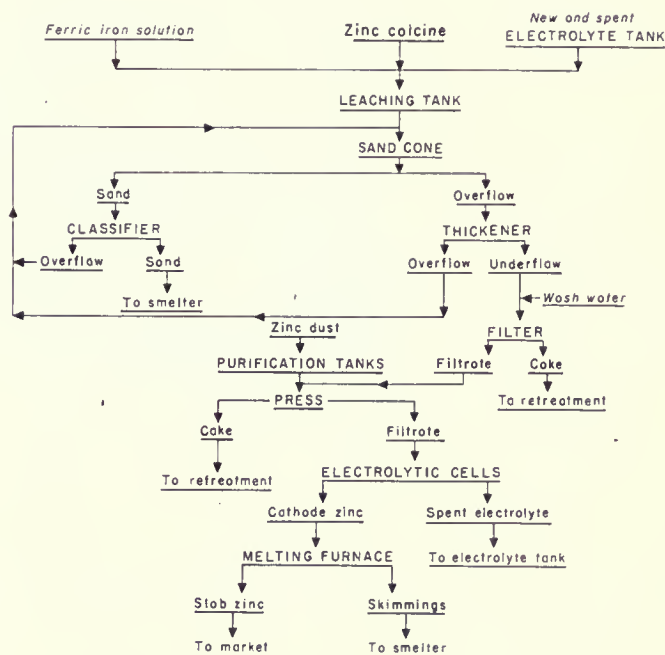
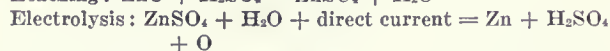
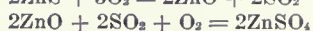
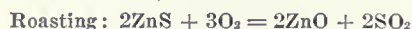


FIGURE 7. Flow sheet of electrolytic zinc plant.



The chemical reactions involved in the roasting, leaching and electrolysis of zinc are as follows:



In 1951, 38 percent of the primary slab zinc produced in the United States was produced by the electrolytic method and 62 percent by distillation methods.

Zinc smelters purchasing California zinc ores or concentrates include the Anaconda Company smelters at Anaconda and Great Falls, Montana, the International

#### Grades of slab zinc.

Grade	Maximum percent allowed				
	Lead	Iron	Cadmium	Total Pb, Fe, Cd	Minimum percent of zinc
Special high grade.....	0.006	0.005	0.004	0.010	99.99
High grade.....	.070	.020	.070	.100	99.9
Intermediate.....	.200	.030	.500	.500	99.5
Brass special.....	.600	.030	.500	1.000	99.0
Selected.....	.800	.040	.750	1.250	98.75
Prime western.....	1.600	.080			98.32

Smelting and Refining Company smelter at Tooele, Utah, and the United States Smelting, Refining and Mining Company smelter at Midvale, Utah.

#### Supply and demand of tons of slab zinc in the United States.

(From Engineering and Mining Journal vol. 156, no. 2, p. 88, Feb. 1955.)

	1953	1954 (Last 2 months estimated)	Change
<b>SUPPLY</b>			
U. S. primary and secondary production.....	971,000	865,000	
Imports.....	227,000	160,000	
	1,198,000	1,025,000	
Less exports.....	18,000	24,000	
Less government account.....	42,000	110,000	
Available for consumption.....	1,138,000	891,000	
<b>CONSUMPTION</b>			
Galvanizing.....	407,000	400,000	—1.7 percent
Die casting and zinc-base alloys.....	307,000	275,000	—10.4 percent
Brass products.....	178,000	102,000	—42.7 percent
Rolled zinc.....	55,000	46,000	—16.4 percent
Oxide plants and other.....	39,000	37,000	—5.4 percent
	986,000	860,000	—12.8 percent
<b>SURPLUS</b> .....	152,000	31,000	

The effects of impurities on the operation of smelters or electrolytic plants require smelter operators to be selective in purchasing materials for treatment. A prospective shipper usually is required to submit a representative sample for analysis, and the material must be judged acceptable before the ore is shipped.

Slab zinc is now produced in six standard grades listed in the accompanying table.

#### The flow of zinc from mine to market. (From the American Zinc Institute, Inc.)

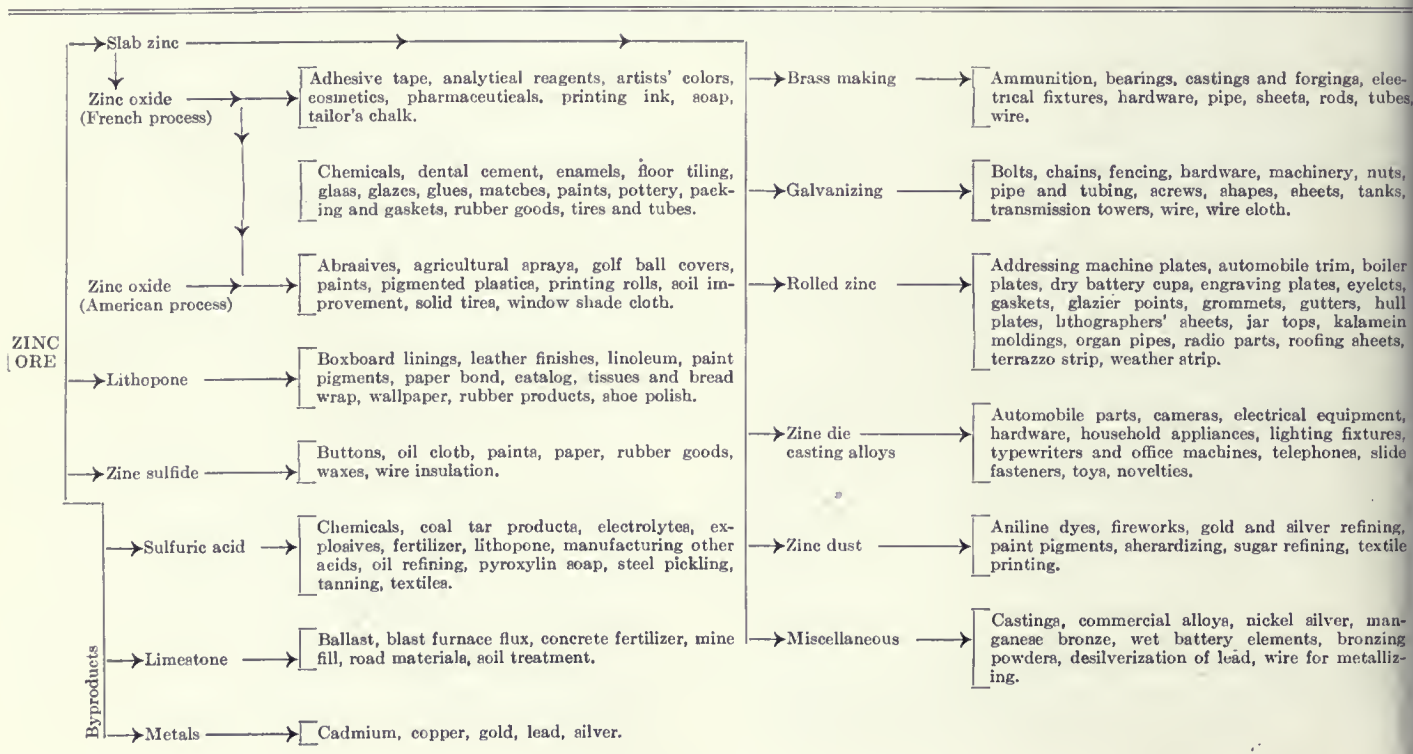






FIGURE 8. Open pit on the Brick Flat ore body of the Mountain Copper Company of California, Shasta County.



FIGURE 9. Diamond drill used to prospect the Brick Flat ore body at Iron Mountain.



*Utilization.* Zinc ranks fourth in tonnage produced among the metals in the United States, being surpassed only by steel, copper, and lead. It is used in an extremely wide range of military and essential civilian products. During World War II the manufacture of brass products accounted for about 50 percent of the consumption of zinc. Galvanizing was the principal use of zinc both before and after World War II. The most impressive change in slab-zinc consumption has been the great increase in the use of zinc for die castings. A summary of the United States slab-zinc supply and consumption for 1954 is given in the accompanying table.

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## ZIRCONIUM AND HAFNIUM

By MELVIN C. STINSON

Zirconium and hafnium occur together in nature. The commercial source minerals, zircon and baddeleyite, are obtained from beach sands and river gravels in the United States, Australia, Brazil, French West Africa, and India.

Zircon is locally abundant in the blank sands and gold placers of California, especially in the Mother Lode region, but the only recorded production of zircon in California was from a dragline dredge near Lincoln, Placer County, in 1937.

Zirconia (zircon oxide) and zirconium compounds that are made directly from zircon and baddeleyite are the principal end products derived from zirconium-hafnium ores. Zircon is used in refractories and foundry sands. Stabilized zirconium oxide is used to insulate high-frequency induction furnaces and to line jet engines. Zirconium metal is used in nuclear reactors, in steel alloys, and in surgery. Hafnium is also used in nuclear reactors.

*Mineralogy and Geologic Occurrence.* The earth's crust contains approximately 0.03 percent zirconium and 0.004 percent hafnium. Hafnium has been found only in zirconium-bearing minerals. Of these, only zircon and baddeleyite are abundant enough to be of commercial interest.

Zircon (zirconium silicate), the most widely distributed and most abundant zirconium mineral, is a common constituent of many igneous and metamorphic rocks and of sands resulting from the disintegration of these rocks. Many sedimentary rocks contain zircon because the mineral is hard and chemically resistant to weathering. Zircon has a hardness of 7.5, a specific gravity of 4.2 to 4.86, a conchoidal fracture, an adamantine luster, and grades from colorless to pale yellow, to brownish-yellow, to grayish-green or reddish-brown. In ultraviolet light, most specimens of zircon fluoresce a brilliant orange, red, or yellow, a phenomenon which has been attributed to the presence of hafnium or uranium in the mineral.

Baddeleyite (zirconium dioxide), much less widely distributed than zircon, occurs in igneous rocks that are deficient in silica, and in sedimentary rocks derived from them. It grades from colorless to yellow, to brown, to black. Baddeleyite has a hardness of 6.5, a specific gravity of 5.5 to 6.0, a conchoidal to uneven fracture, and a greasy to vitreous luster.

The zirconium-hafnium content of igneous and metamorphic rocks rarely exceeds 0.06 percent. These elements are not known to be concentrated in veins, but the high specific gravity of zirconium minerals leads to their concentration in placer deposits. As the expense of removing zirconium- and hafnium-bearing minerals from hard rocks is much greater than from placer deposits, and as placer deposits commonly are richer in such minerals, the commercial production of zirconium and hafnium has been obtained only from sands.

Nearly all of the zirconium used in American industry is obtained from three extensive placer deposits, one each in Florida, Australia, and Brazil. The deposits in Florida and Australia consist of Recent sea-coast sands from which zircon and other heavy minerals such as

rutile, monazite, and ilmenite are readily separated. The Brazilian deposits contain a variety of baddeleyite known as "brazilite," and brazilite-zircon, a mixture which is marketed as "zirkite." The deposits occur in the Plateau of Pocos de Caldas in the southwestern part of the Minas Gerais. Although in the past, large tonnages of baddeleyite have been imported from Brazil, at present, this is a much less important source than Florida. Zircon has been produced during monazite dredging in Idaho but has not been marketed because of unfavorable freight rates and a lack of western markets.

Occurrences of zircon have been noted in many placer gold deposits in California, but only one has yielded zircon on a commercial basis. This zircon was recovered in a dragline gold dredging operation in 1937 near Lincoln in Placer County. The concentration of zircon in California sands is generally too low to permit the commercial recovery of this mineral at the current prices and with the limited western market.

A detailed study of the minerals found in black sands (Day and Richards, 1906, pp. 1175-1258) included placer deposits in most of the western states including California. This study provided the data on zircon concentrations in California placer deposits, as reproduced in table 1.

Table 2 shows the approximate amount of zircon found by the U. S. Bureau of Reclamation in stream-bed sands of some of the San Joaquin Valley rivers and creeks.

*Utilization.* Zircon consumption in the United States in 1953 was estimated at 45,000 tons. In 1953 the distribution by uses was as follows: refractories, 28 percent; foundry facings, foundry sand, and blasting grain, 27 percent; pottery, porcelains, enamels, and glazes, 20 percent; metal and alloys, 12 percent; chemicals and salts, 6 percent; glass, 2 percent; miscellaneous, 5 percent (Griffith, 1953, p. 4).

Zircon is used extensively in manufacturing refractory materials because of its high melting and softening points, good thermal conductivity, low thermal expansion, good abrasion resistance, and high resistance to certain molten metals, corrosive chemicals, slags, and glasses. In the aluminum industry, zircon bricks are used in constructing reverberatory or open-hearth furnaces because zircon shows non-wetting characteristics toward the molten metal. The high specific gravity of zircon is advantageous in that it prevents broken pieces of refractory from floating in the metal and appearing as defects in the casting. Zircon discharge spouts for smelters also have proved very satisfactory.

Zircon crucibles are used in melting platinum, platinum alloys, and palladium. Zircon sand, flour, and washes have had wide usage in steel, iron, bronze, aluminum, and magnesium foundries. The high refractoriness and slight chilling effect make zircon highly effective in combating "burning in." The chilling effect of zircon is caused largely by a higher thermal conductivity than that of silica sand. The low and uniform expansion of zircon when compared with silica decreases the cracking of cores and molds during the baking and pouring



Table 1. Concentration of zircon in black sand samples from placer deposits in California (modified after Day and Richards).

Locality	Zircon (lbs. per ton of black sand)	Remarks	Locality	Zircon (lbs. per ton of black sand)	Remarks
Butte County			Placer County		
Nimshew.....	1		North Fork American River.....	340	50 lbs. black sand per ton of gravel
Oroville.....	48		Gold Run.....	192	½ lb. black sand per cu. yd. gravel
Oroville.....	4	Black sand from dredge clean-up	Gold Run.....	202	½ lb. black sand per cu. yd. gravel
Sterling City.....	22	Concentration not known	Plumas County		
Sterling City.....	52	Black sand from sluice box	Spanish Ranch.....	20	9 lbs. black sand per ton of gravel
Cherokee.....	20	Old tailing dump (fine sand), panning	Rock Island Hill.....	88	Concentration not known
Cherokee.....	372	Pannings from old dump			
Cherokee.....	230		Riverside County		
Little Rock Creek.....	184	Very plentiful; ground sluicing	Holcomb.....	40	12 lbs. black sand per cu. yd. gravel
Brush Creek.....	20	4 lbs. black sand per cu. yd. of gravel			
Calaveras County			Sacramento County		
Douglas Flat.....	64	Concentrated from 60 tons to 100 lbs.	Michigan Bar.....	316	Concentration not known
Wallace.....	128	Concentration not known	San Luis Obispo County		
Del Norte County			Beach sand.....	30	Natural sand
Crescent City.....	44	Natural sand, not concentrated	San Francisco County		
Crescent City.....	20	Natural sand, not concentrated	Beach sand.....	2	
Gilbert Creek.....	1	Natural sand, not concentrated			
Gilbert Creek.....	19	Heavy tailings from sluice box	San Mateo County		
Smith River.....	18	Heavy tailings after gold removed by sluicing.	Beach sand.....	100	Natural sand
El Dorado County			Santa Barbara County		
Brownsville district.....	80	1 lb. of black sand from 7 cu. yds. gravel	Point Sal.....	54	Not concentrated
Placerville.....	176		Point Sal.....	94	Concentrated from sluice box
Grizzly Flats.....	16	1 lb. of black sand per ton gravel; sluicing	Santa Cruz County		
Humboldt County			Aptos.....	26	Natural sand
Gold Bluff.....	17	Selected streak of beach sands	Aptos.....	18	Natural sand
Gold Bluff.....	17	Tailings from above	Aptos.....	22	Natural sand
Gold Bluff.....	3	Ordinary beach sand	Aptos.....	24	Natural sand
Gold Bluff.....	2	Beach sand	Shasta County		
Gold Bluff.....	6	Beach sand	French Gulch.....	24	Concentration not known
Gold Bluff.....	16	Beach sand	Redding.....	40	½ lb. black sand from 5 tons gravel
Gold Bluff.....	6	Beach sand	Redding.....	32	Concentration not known
Gold Bluff.....	10	Beach sand			
Gold Bluff.....	14	Concentrated by panning beach sand	Siskiyou County		
Upper Gold Bluff.....	12	Beach sand concentrates	Callahan (Grouse Creek).....	50	1 lb. black sand from 16 cu. yds.; ground sluicing
Orleans.....	4	Heavy sand in sluice boxes	Cecilville.....	6	Concentration not known
Trinidad.....	80	Beach sand, 3 feet below surface	Forks of Salmon.....	140	Waste material from clean-up
Los Angeles County			Sawyers Bar.....	60	Pannings from sluice-box tailings
Ocean Park.....	2	Beach sand	Scott River.....	50	1 lb. black sand from 10 cu. yds. gravel
Mendocino County			Trinity County		
Fort Bragg.....	34	Not concentrated	Trinity Center.....	100	Concentration not known
Fort Bragg.....	5	Not concentrated	Burnt Ranch.....	350	4½ lbs. black sand per cu. yd. gravel
Nevada County			Junction City.....	32	Hydraulic tailings
Rough and Ready.....	14	Concentration not known	Carrville.....	25	40 lbs. black sand per ton of gravel
Rough and Ready.....	50	Heavy sand from hydraulic clean-up	Yuba County		
Nevada City.....	928	Old river channel	Camptonville.....	40	1 lb. black sand per 3 cu. yd. of gravel

cycles, tending to eliminate the formation of fins on castings.

Zirconia ( $ZrO_2$ ), used as an insulating material between the crucible and coils in induction melting, increases the life of the crucible by decreasing the thermal shock caused by the difference in temperature between the top and bottom of the crucible. Because of crystal inversions, pure zirconia alone is of little value as a commercial refractory; it breaks to pieces within a few heating and cooling cycles. If about 4½ to 6 percent calcium oxide is introduced into the crystal, however, it changes from the unstable monoclinic form to a stable cubic form.

Stabilized zirconia, applied as a wash to zircon induction furnace linings, has greatly increased their life and is especially helpful in preventing slag build-up. The life of magnesia crucibles also has been considerably length-

ened by applying a wash of zirconia to the inner surface. Zirconia is also used for lining jet engines.

Zircon and zirconia products formerly were important materials in porcelain enamel, but the development of titanium dioxide opacified enamels reduced this use considerably. Zirconia has been extensively used as an opacifier to replace the more expensive tin oxide. In the preparation of coloring oxides, used in producing colored enamels, zirconia products are often used for toning or producing lighter shades.

The use of zircon and zircon products as opacifiers for whiteware glazes is well known. Zirconium opacifiers also produce craze resistance and scratch hardness.

Clay, alkaline earth oxides, and zircon are used as raw materials in a zircon porcelain which has excellent thermal shock resistance as well as desirable electrical properties and high mechanical strength. This porcelain



Table 2. Approximate amount of zircon in sand from recent streams in the San Joaquin Valley (Data from U.S. Bur. Reclamation, Ground Water Inv., Friant-Kern service area, San Joaquin Valley, California, 1953).

Stream	Total heavies in sand (%)	Zircon in heavies (%)	Pounds of zircon per ton of sand
San Joaquin River	6.60	0.288	0.38
Kings River	14.35	0.812	2.4
Kaweah River	11.31	0.574	1.26
Tule River	15.41	0.511	1.58
Deer Creek	8.35	0.232	0.38
Poso Creek	6.05	3.24	3.92
Kern River	7.19	0.616	0.89
Kern River	23.59	1.406	7.2
Salt-Tecuyah Creeks	2.0	3.136	1.26
Plieto Creek	3.94	2.205	1.66
San Emigdio Creek	7.96	1.556	2.48
Sandy Creek	10.72	4.491	9.62

is used in such items as switch parts, coil forms, rheostat assemblies, insulating washers, spark plugs, and electrical insulation.

The high mechanical strength and high electrical resistivity of zircon at high temperatures has led to the use of zircon shapes and zircon electrical cements for high temperature electrical insulation. Zircon circuit breakers and arc chute plates have proved very satisfactory.

In the glass industry, zircon and zirconia products are used in low-porosity zircon refractories that are particularly well suited for use in contact with molten glass. In special glass compositions, such as the glass that is used for glass to metal seals, zircon and zirconia are being used as components of the glass batch. Zirconia as a lens polishing compound is replacing the higher priced ceria products. Zirconia has also partly replaced the less expensive rouge as a polishing agent because it provides higher polishing efficiency, greater glass removal, and cleaner polishing. Zircon is used in the abrasive industry as abrasive grains and also as a component of vitrified grinding wheel bonds.

Zirconia is used as a batch component in the preparation of coatings for welding rod used to weld free machining, high sulfur steels and armor plate.

The earliest use of zirconium metal, which was produced as a powder, was for priming explosives and flashlight powders. Zirconium powder is extremely combustible and produces a very bright light when ignited. Zirconium metal possesses a strong affinity for oxygen and nitrogen at elevated temperatures and for this reason is used as a "getter" in radio tubes.

Most of the zirconium used in the metals industry is in the form of zirconium ferrosilicon in steels and other alloys. In steel-making, zirconium acts as a powerful deoxidizer and as a scavenger of nitrogen and sulfur. It also promotes depth-hardening ability in the heat-treated engineering steels. Zirconium is also used as an alloying material in the manufacture of gray cast iron to improve the machinability.

Hafnium-free ductile zirconium metal is used as a construction material in Government-sponsored nuclear-reactor plants. Among the metals only beryllium, bismuth, and magnesium have a lower thermal-neutron absorption cross-section (ability to absorb neutrons)

than zirconium. Such absorption is wasteful of the available energy in uranium, thorium, and other fissionable material.

The excellent corrosion resistance of zirconium metal probably will result in one of its most useful applications. It resists corrosion by most of the organic acids, metal chlorides, and especially hydrochloric acid and phosphoric acid. It is, therefore, suitable for surgical equipment, such as pins, screws, and plates for bone repairs, suture wire, and instruments.

The use of zirconium salts and chemicals has been expanding rapidly since 1950. Zirconium carbonate and zirconium hydroxide are used in poison ivy ointment and in personal deodorants. Wax emulsions mixed with zirconium acetate or ammonium zirconyl carbonate form good water repellants for textiles. Zirconium salts are used to precipitate either acid or basic dyes on textiles. Zirconium phosphate is used to treat stomach ulcers.

Small quantities of hafnium have been used in carbide cutting tools, fluorescent powders, and for alloying with the tungsten filaments of electric incandescent lamps to increase their strength. Hafnium has become prominent in the atomic energy field as a material for control devices in nuclear reactors. Because of its very high capture cross-section, hafnium control rods are used to adjust the reactivity of the reactor core. With the control rods completely inserted in the core, the high thermal-neutron-absorption of the hafnium will prevent the chain reaction from starting (Goodwin, p. 1162).

*Mining Methods and Treatment.* Zircon-bearing placer deposits are worked by strip mining or conventional dredging methods. Such methods employ stripping equipment and transport conveyors or bucket-line, suction, or drag-line dredges. The method used to recover the zircon from the heavy concentrate depends largely upon the nature of the other minerals. Magnetic or electrostatic separation or a combination of the two are usually employed to remove the other heavy minerals because zircon is non-magnetic and a poor conductor of electricity.

In Australia, a maximum of 20 feet of overburden is removed by bulldozer or draglines. The heavy mineral seams thus exposed are mined either by selective hand-shovelling into trucks or by diesel shovel, scoop, or other power driven machinery. The sand containing the heavy minerals is hauled by truck to the treatment plant where silica is removed from the heavy minerals by means of concentrating tables or Humphreys spirals. The heavy fraction is then run through a series of electrostatic and magnetic separators to separate rutile, ilmenite, and monazite from the zircon (figure 1).

The Brazilian zirconium ore occurs in alluvial, eluvial, and vein deposits (Miller, 1954, p. 9). The highest grade material consists of large pebbles in the gravels. Mining is by picks and shovels. Most of the ore is obtained from surface concentrations but some is mined from pits up to 60 feet in depth. All the vein material is transported to washing plants and concentrated by sluicing, sieving, hand-picking, and hand-jigging.

The zirconium-bearing beach deposits in Florida are mined with a floating suction dredge. The sands are pumped to a battery of Humphreys spirals from which heavy-sand concentrates are obtained. These are put



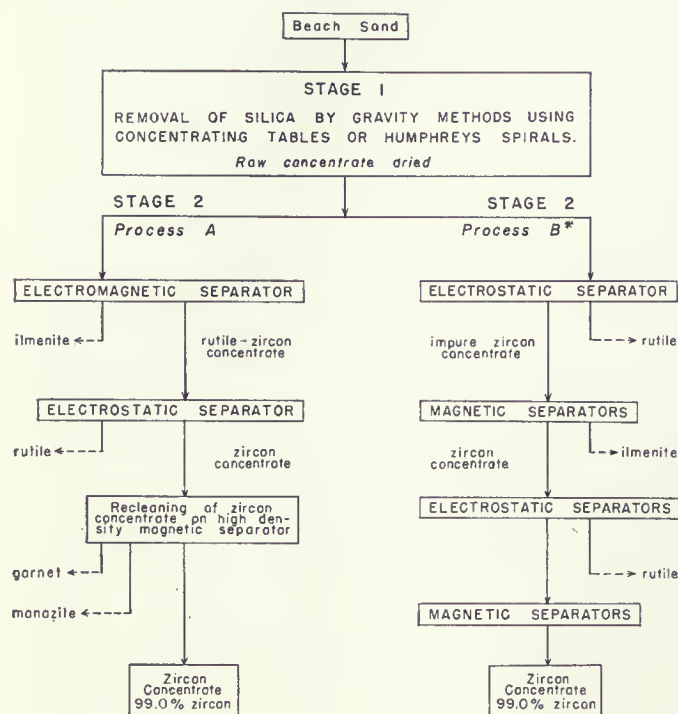


Fig. 1 Flow sheet for Australian Beach Sand Concentration  
(From Chem. Eng. and Mine Rev., June 10, 1955, p. 336)  
\*Process B was the method in general use in 1955.

FIGURE 1. Flow sheet for Australian beach sand concentration.  
(From Chem. Eng. and Min. Rev., June 10, 1955, p. 336.)

through a large electrostatic separator to separate the titanium-bearing minerals from the other less conductive material which includes zircon. The zircon-bearing rejects are again run through the Humphreys spirals to remove the remaining quartz and other silicates. The concentrates are passed over a magnetic separator and a clean zircon product is obtained in the tailings.

The zircon that has been recovered as a by-product of monazite production in Idaho is being stockpiled pending the development of a western market. The zircon-bearing placer material is mined by bucketline dredges. After the larger material is removed by screening, the sand is passed over two batteries of jigs. The concentrates from the jigs are shipped to the separating plant where they are dried and passed over electrostatic separators, magnetic separators, and an induced magnetic roll. The zircon remains in the tailing product along with any silicate minerals not removed by the jigs on the dredge.

Zirconium and hafnium can be recovered from the concentrates by several methods, but only two commercial processes, the Kroll (magnesium-reduction) and the van Arkel-de Boer (iodide) yield metals pure enough to be ductile. In both processes, the zirconium- and hafnium-bearing material must be decomposed. For the silicate (zircon), this is a difficult task. The decomposition involves: (a) removal of silica by volatilization, (b) sintering and digesting with acid, (c) fluxing with alkalis, (d) carburizing followed by direct chlorination or

hydrofluoric acid treatment and fluoride fusion followed by chlorination. Zirconium tetrachloride, the end product of the direct chlorination method, is the starting compound of the Kroll process. In the Kroll process, molten magnesium is used to reduce zirconium tetrachloride in an inert atmosphere of argon or helium.

The material produced by the Kroll process varies considerably in its impurity content and consequently in the physical properties of each batch. The Kroll sponge can be refined by means of the van Arkel-de Boer iodide process which involves the use of crude zirconium to form a volatile zirconium iodide and the subsequent decomposition of the iodide on a heated zirconium filament. By this process, a pure, ductile, corrosion-resistant, crystal-like solid mass of zirconium called "crystal bar" is made.

If the zirconium is to be used in nuclear reactors where a hafnium-free material is needed, the zirconium should be recovered from zirconium oxide obtained from the hafnium-separation process (Lustman and Kerze, p. 205) in which the zirconium oxide is reduced directly with aluminum, calcium, or magnesium. The resultant material, which is impure, is used to feed the van Arkel-de Boer iodide-decomposition unit.

Zirconium and hafnium are so similar, both in their occurrence and chemical behavior, that methods used to free zirconium will, at the same time, free hafnium. In order to produce pure hafnium, the zirconium must be removed.

The production of hafnium as developed at the Northwest Electrodevelopment Laboratory of the U. S. Bureau of Mines, Albany, Oregon, consists of the following steps (Holmes, Barr and Gilbert, 1955, p. 9): (1) Separation of hafnium compounds from zirconium ores, (2) Converting the hafnium to the oxide, (3) Direct chlorination of hafnium oxide, (4) Purification of hafnium tetrachloride, (5) Reduction of refined hafnium tetrachloride with magnesium metal, (6) Removal of magnesium chloride (formed in the reduction process) and the excess magnesium from the hafnium by treatment in a vacuum distillation step, (7) Cleaning and crushing of the sponge in preparation for further treatment.

**History of Production.** Before World War I the use of zirconium and its compounds was largely experimental and confined almost entirely to Germany and Austria. Small lots of zirconium ore had been produced in the United States (the first of 1,000 pounds in 1869) for use in the manufacture of incandescent gas mantles. In 1906, the discovery of large quantities of baddeleyite in Brazil led to the extension of uses of zirconium by German chemists. The Germans were credited with producing a remarkable zirconium steel which was claimed to be much superior to other alloy steels. During World War I, the United States Government investigated the German claims, but did not confirm their reported findings. However, these and subsequent investigations of the effects of zirconium on steel and other alloys resulted in considerable usage of zirconium alloys as deoxidizers and addition agents.

In 1925, a significant advance came with the development, by van Arkel and de Boer, of the iodide process for refining zirconium and other metals. This process was slow and expensive, but was used until 1947 when Kroll



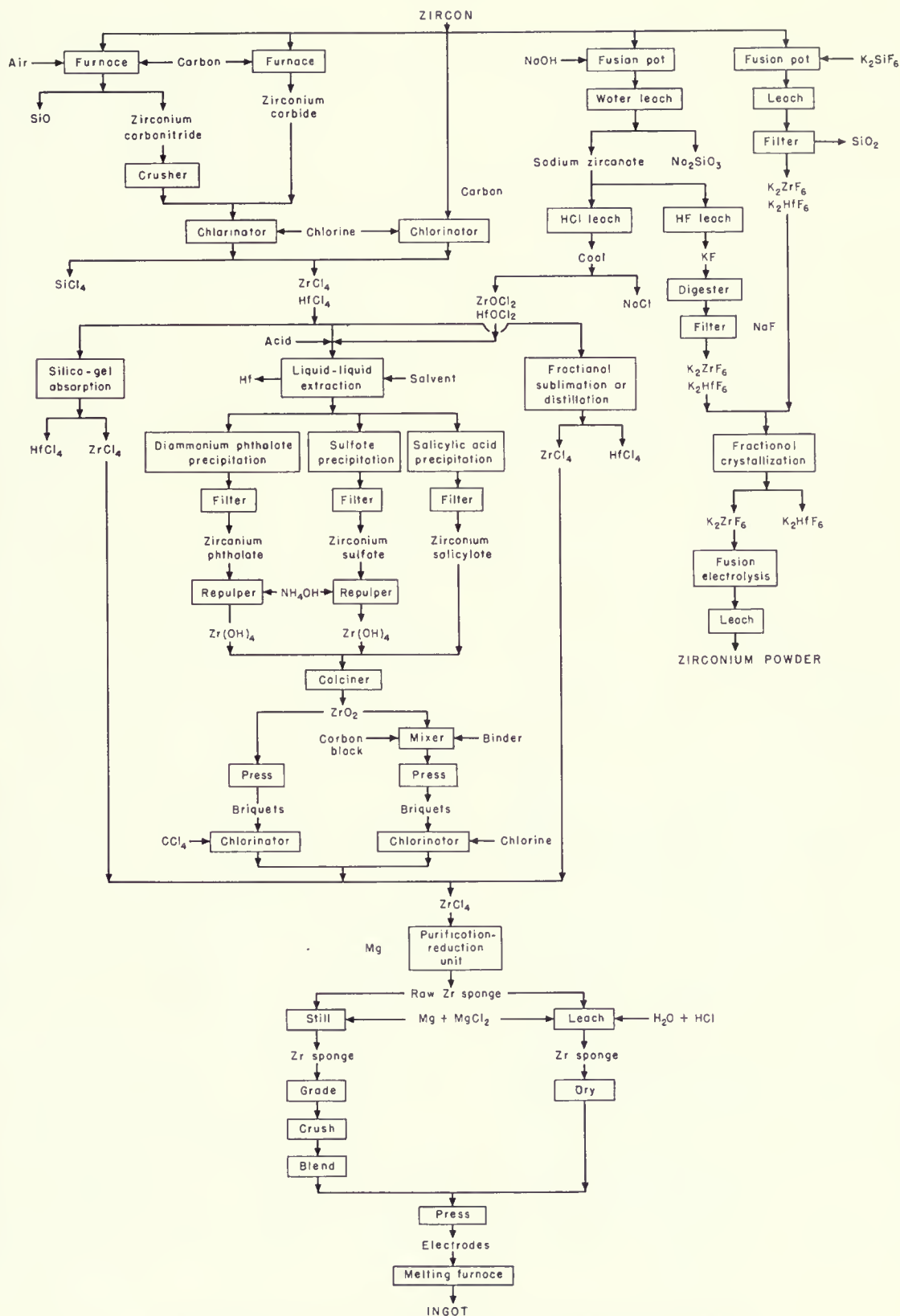


FIGURE 2. Flow sheet for Kroll process. (After Lustman and Kerze.)



adapted his titanium-magnesium reduction process to the production of zirconium.

In 1948, an extensive effort was started to determine an economical means for the removal of hafnium which had been isolated in 1931. At the same time (1948) reactor studies were begun to determine how, where, and to what extent zirconium could be effectively used in the atomic energy program. Zirconium showed promise of considerable superiority over aluminum as a structural material because of its greater resistance to corrosion. This would permit use of higher water-coolant temperatures, which would increase the heat-transfer rates and efficiency of power production. After additional investigations in 1949, with favorable results, zirconium was chosen by the Power Pile Group of the Oak Ridge National Laboratory as the structural metal for the Submarine Thermal Reactor. This decision greatly stimulated the production and development of zirconium (Lustman and Kerze, p. 4). Since 1950, the United States Bureau of Mines, the Reactor Division of the Atomic Energy Commission, and the Oak Ridge National Laboratory have made many studies of zirconium. These have resulted in more efficient hafnium separation methods, cheaper and purer sponge zirconium, and much data on alloys, fabrication, and physical and mechanical properties. One direct result of these studies is the lowering of the cost of zirconium and zirconium compounds and hafnium. With a decrease in cost of zirconium, industrial interest in zirconium has continued to rise.

Until very recently, hafnium was produced in laboratory quantities only. However, with the discovery of new and cheaper methods of separating hafnium from zirconium, the production of hafnium should increase and new uses of hafnium be found.

**Markets.** The United States is the largest consumer of zircon and baddeleyite. Practically all the zirconium ore imported into the United States comes from either Australia or Brazil and is unloaded at ports on the Atlantic seaboard. The quantity of zircon imported from Australia was comparable to United States mine production in 1954, although domestic mine-production capacity is reported to be capable of meeting domestic requirements. Apparently, a favorable price differential and a tie-in with rutile imports, a mineral in short supply, accounted for the large United States consumption of Australian zircon in preference to the domestic product (Griffith, 1955, p. 7).

Engineering and Mining Journal Metal and Mineral Markets quoted zircon concentrates (65 percent  $ZrO_2$  minimum) c.i.f. Atlantic ports, at \$47.00-\$48.00 per long ton throughout 1954. Because zircon contains a theoretical 67 percent  $ZrO_2$ , at least a 97 percent zircon concentrate is necessary to achieve the specified 65 percent  $ZrO_2$  content. Zirconium sponge was listed at \$10.00 per pound and zirconium crystal bar at from \$70.00 to \$90.00 per pound depending upon the quantity ordered. Hafnium metal powder was quoted at \$25.00 per gram in 1953 (Griffith, 1955, p. 7).

The principal market for zircon in California is for use as a foundry sand. The current price for Australian zircon sand containing 65 percent  $ZrO_2$  is \$65.00 per ton in 5-ton lots (delivered in Los Angeles). Zircon sand from Idaho may be obtained in Los Angeles for \$55.00-\$60.00 per ton in 50-ton carload lots. This sand is coarser than Australian zircon and contains some garnet. The amount of zircon sand used by the foundry industry in northern California cannot be closely estimated; however, it probably exceeds 500 tons per year.

The Atomic Energy Commission recently announced (Los Angeles Times, May 7, 1956) award of contracts for 11,000,000 pounds of zirconium to be delivered over a five-year period at a total cost of about \$75,000,000. One of the three companies which received a contract is the National Research Corporation with a plant near Pensacola, Florida. National Research Corporation reported its price on zirconium will be \$6.50 a pound. The other companies are expected to receive about the same price per pound. Prior to the new procurement, the price of reactor grade zirconium was \$14.00 a pound.

The major deterrents to the establishment of zircon production in California may be summarized as follows: (1) The concentration of zircon is generally not high enough to compete, under present economic conditions, with foreign sources of zircon (at present, there is no western market for most of the heavy minerals which may be recovered with zircon), (2) High cost of transportation to eastern markets, (3) Lack of western manufacturers of zirconia (zircon oxide) refractories and ceramic materials, (4) No western zirconium metal plants except U. S. Bureau of Mines plant at Albany, Oregon, (5) The hafnium content of all California zircon tested to date is only average (1 to 2%).

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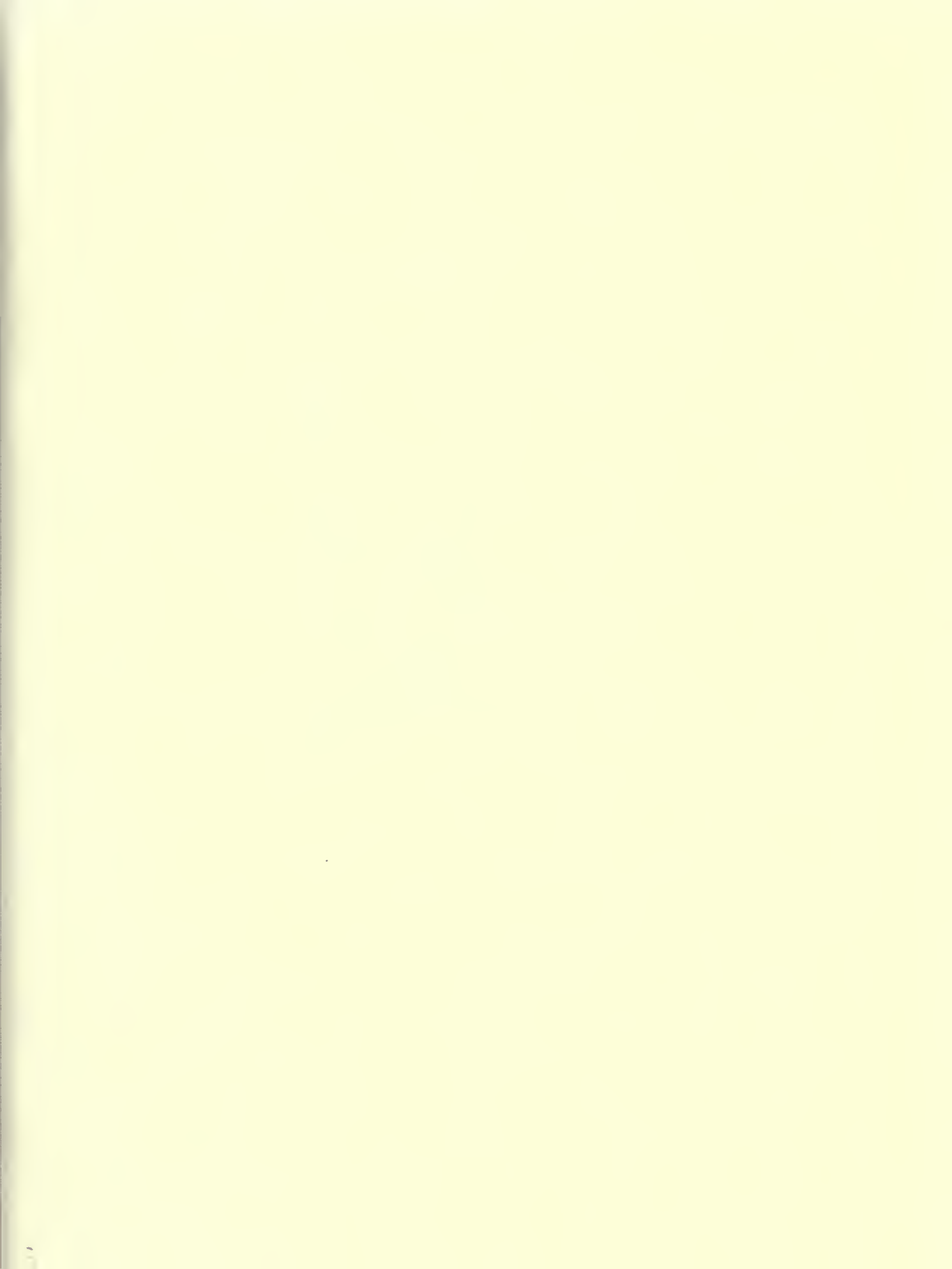
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